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**A KINETIC MODEL AND COMPUTER SIMULATION  
FOR A PULSED DF-CO<sub>2</sub> CHEMICAL TRANSFER  
LASER**

**Ronald L. Kerber, et al**

**Aerospace Corporation**

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# A Kinetic Model and Computer Simulation for a Pulsed DF-CO<sub>2</sub> Chemical Transfer Laser

Prepared by  
R. L. KERBER, N. COHEN, and G. EMANUEL  
Aerophysics Laboratory

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THE AEROSPACE CORPORATION  
El Segundo, California

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Los Angeles, California

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## FOREWORD

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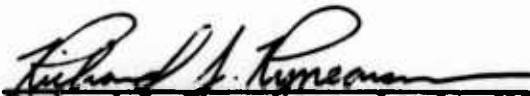
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W. R. Warren, Jr., Director  
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**KEY WORDS****Chemical Kinetics****Chemical Laser****CO<sub>2</sub> Laser****Computer Modeling****Energy Transfer Reactions****Distribution Statement (Continued)****Abstract (Continued)**



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## I. INTRODUCTION

Evaluation of the performance of gas and chemical lasers requires an understanding of the kinetic and chemical mechanisms that pump and deactivate the energy levels associated with lasing. Normally, a simple model may be constructed that explains why lasing occurs for a particular species. However, a more detailed representation of the mechanisms is needed for an accurate prediction of laser performance. Recently, comprehensive theoretical models for computer simulation of laser performance have been developed [1-4] that utilize a detailed formulation of the kinetics of the lasing system. A review of the kinetics for the  $\text{CO}_2\text{-N}_2$  laser system is given by Taylor and Bitterman [5]; Cohen [6] gives a similar review for the  $\text{H}_2\text{+F}_2$  chemical laser. With the discovery and development [7-16] of the  $\text{DF-CO}_2$  chemical transfer laser, it is desirable to assemble a kinetic model that will facilitate future studies of this laser.

This report presents the results of our efforts to gather and compile a complete set of the required rate coefficients based on data available in the literature, comparisons with similar reactions with known rate coefficients, or various theoretical approaches. We have drawn heavily on Refs. [5] and [6]; we include data prior to those studies only when necessary.

A schematic of the  $\text{DF-CO}_2$  transfer and the  $\text{CO}_2$  kinetics is shown on an energy level diagram in Fig. 1. The vibration-translation (VT) energy transfer reactions are denoted by dotted lines; intramolecular vibration-vibration (VV) reactions are shown as solid lines; and the intermolecular VV

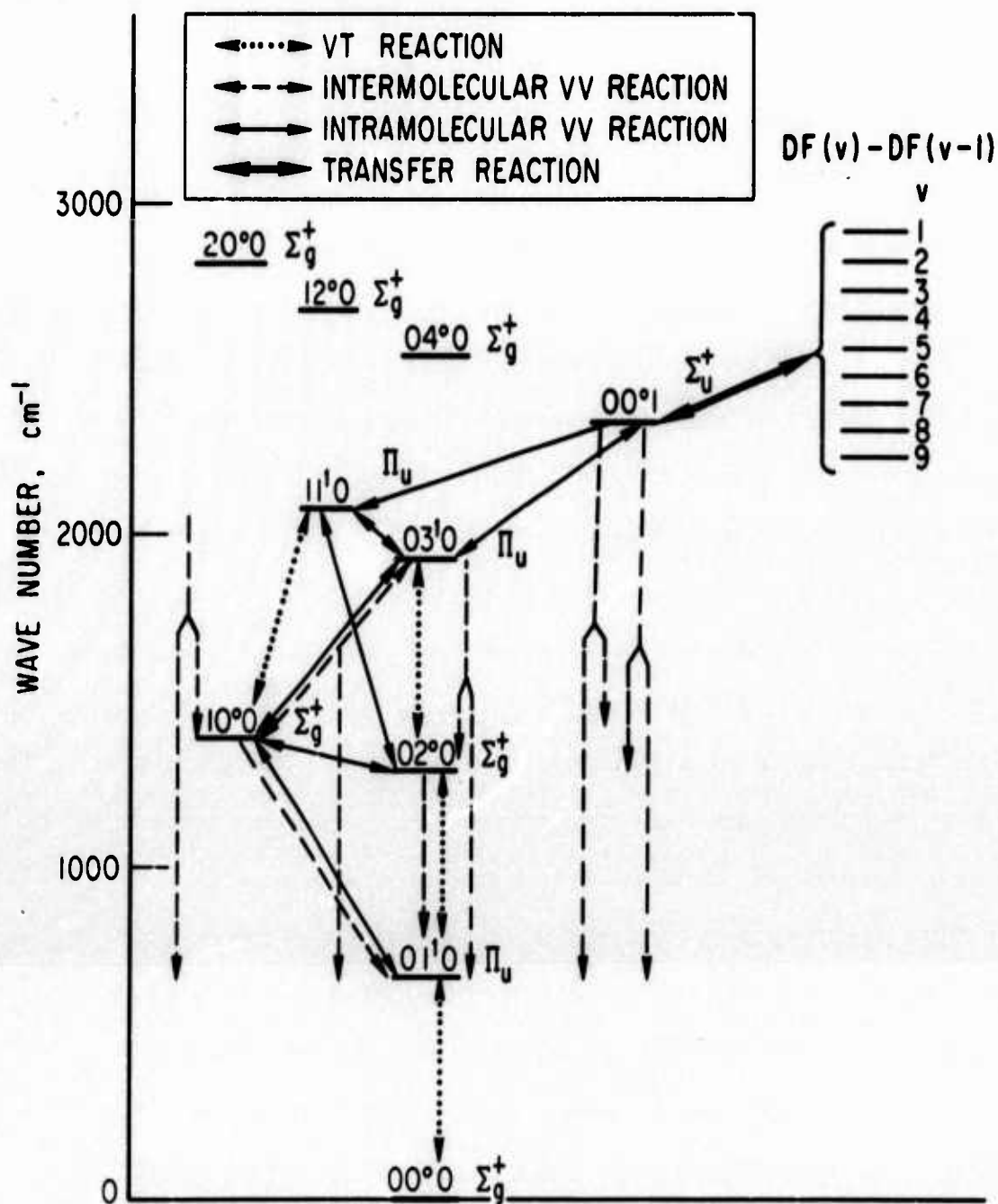


Fig. 1. Vibrational energy level diagram for CO<sub>2</sub> kinetics including the DF transfer energy. The states (03<sup>3</sup>0) and (02<sup>2</sup>0) are deleted for clarity. These states are included in the model.

transfer reactions are denoted by dashed lines with arrows to the final states. Initial states of these intermolecular VV reactions are  $\text{CO}_2(00^00)$  and the  $\text{CO}_2$  state at the tail of the dashed arrow. The states  $(03^10)$  and  $(03^30)$  are assumed to be in equilibrium and are statistically combined as  $(030)$ . Reactions involving the state  $(02^20)$  are similar to those for  $(02^00)$  but have been omitted from the figure to preserve clarity.

We limit our model to energy levels in  $\text{CO}_2$  below  $\text{CO}_2(00^01)$ ; for comparison, Fig. 1 shows three higher states. This limitation is artificial; however, we expect levels above  $(00^01)$  to play a minor role in transfer laser performance. We assume DF to transfer only to  $\text{CO}_2(00^01)$ . The net effect on laser performance of transfer to levels higher than  $\text{CO}_2(00^01)$  and their ultimate deactivation to  $(00^01)$  should be small.

The laser simulation program used in this study utilizes rate coefficients of the form [2]

$$k = AT^D e^{-E/RT}$$

where A and D are constants, E is the activation energy, R is the gas constant, and T is the temperature. All rate coefficients are presented in this form. The proposed kinetic model is used with this program to determine the relative importance of kinetic mechanisms during a pulse for two different initial F atom concentrations. This model has proven successful in the prediction of characteristics of the HF pulsed laser [17]. A number of rate coefficients are roughly approximated; therefore, they are varied to determine the sensitivity of laser performance to their values under typical laboratory

conditions. This sensitivity study shows that the peak pulse power and pulse energy are sensitive to the  $F_2 + D_2$  pumping reactions and to the temperature dependence of the  $DF(v)-CO_2$  transfer rate coefficient and its variation with  $v$ . The temperature variation of the rate of VT deactivation of  $CO_2(00^0 1)$  by DF and the DF-F and DF-D VT processes are also important in predicting laser performance. For the reactant mixtures studied, the rate of equilibration of the lower levels in  $CO_2$  is so fast that they are near equilibrium, and thus modeling is insensitive to the value of rate coefficients for these levels.

In Section II, we review the kinetics for the  $D_2 + F_2$  system, which may be used for modeling the DF chemical laser. Sections III and IV review the kinetics of DF -  $CO_2$  vibrational energy transfer and the kinetics of  $CO_2$  relaxation, respectively. Section V describes the computer experiments, and Section VI gives a brief summary of the work.



## II. THE $D_2 + F_2$ KINETICS

Theoretical and experimental studies of the kinetics of  $H_2 + Cl_2$  and of  $H_2 + F_2$  mixtures have been made to test proposed theories and increase our understanding of the underlying processes. We draw heavily on these and analogous mixtures for modeling of  $D_2 + F_2$  kinetics when direct experimental measurements are not available.

### A. RECOMBINATION - DISSOCIATION REACTIONS

The initiating step in the exothermic chemical reaction is usually dissociation of  $F_2$  or  $D_2$ . Conversely, the recombination of D and F with themselves or each other represents a potential energy loss mechanism for laser systems. Under typical operating conditions, these reactions have little or no effect on laser performance; however, we include them for completeness. For the dissociation rate of  $F_2$ , we use the rate coefficient given by Ref. [6],



$$k_1 = 5 \times 10^{13} e^{35.30}$$

where M is all collision partners. All rate coefficients are given in units of cc/mole-sec and  $\theta = -10^3/RT$ . The recombination rate data of Jacobs, Giedt, and Cohen [18] for React. (2) are used:



where

$$k_{-2} = 10^{18} T^{-1}$$

for M equals all species except  $D_2$  and D. For  $D_2$  and D, this rate is increased by a factor of 1.75 and 20, respectively. The minus subscript indicates a backward rate. The populations in the higher levels of  $D_2(v)$  are small and are not included in React. (2).

The rate of dissociation of HF has been measured by Jacobs, Giedt, and Cohen [19]. We take their rate coefficient for DF dissociation by all species



with

$$k_3 = \frac{1.2 \times 10^{19}}{n} T^{-1.0} e^{-(D^* - E_v)/RT}$$

where  $D^*$  (137.13 kcal) is the dissociation energy of  $DF(0)$ ,  $E_v$  is the vibrational energy above ground state, and  $n$  is the number of vibrational levels considered, here taken as 10. The factor  $1/n$  is used so that the total recombination rate is in agreement with experiment; thus, all rates of recombination have equal probability. The vibrational energy for level  $v$  is computed from data given by Herzberg [20]. The enthalpies of formation are listed in Table I for all species included in our model.

Table I. Enthalpy of Formation of Included Species

Species	$\Delta H_f^0$ (kcal/mole)	Species	$\Delta H_f^0$ (kcal/mole)
DF(0)	-64.98	CO <sub>2</sub> (00 <sup>0</sup> 1)	-87.331
DF(1)	-56.67	CO <sub>2</sub> (11 <sup>1</sup> 0)	-88.111
DF(2)	-48.62	CO <sub>2</sub> (030)	-88.531
DF(3)	-40.83	CO <sub>2</sub> (10 <sup>0</sup> 0)	-90.081
DF(4)	-33.29	CO <sub>2</sub> (02 <sup>2</sup> 0)	-90.236
DF(5)	-26.00	CO <sub>2</sub> (02 <sup>0</sup> 0)	-90.381
DF(6)	-18.95	CO <sub>2</sub> (01 <sup>1</sup> 0)	-92.141
DF(7)	-12.13	CO <sub>2</sub> (00 <sup>0</sup> 0)	-94.051
DF(8)	- 5.56	D <sub>2</sub> (0)	0.00
DF(9)	0.786	D <sub>2</sub> (1)	8.544
F	18.9	D <sub>2</sub> (2)	16.764

## B. CHEMICAL PUMPING REACTIONS

The overall rate coefficients of the chemical pumping reactions



and



have been calculated to be  $10^{13.79} e^{1.46\theta}$  and  $10^{14.24} e^{2.4\theta}$  by Wilkins [21] using absolute reaction rate theory. An overall rate of  $10^{13.8} e^{2.16\theta}$  for  $k_4$  has been obtained by Jaffe and Anderson [22] from a limited number of classical trajectory calculations. In addition, Monte Carlo calculations by Muckerman [23] indicate that the overall rate for React. (4) is about 0.6 times that of  $\text{F} + \text{H}_2$ , in agreement with Ref. [22] and the calculations of Wilkins [24].

On the basis of heats of formation in Table I, these reactions release 30.63 and 99.33 kcal/mole, respectively, for  $v = 0$ . The distribution of this energy among the vibrational levels of  $\text{DF}(v)$  for React. (4) has been measured by Parker and Pimentel [25] at 390°K, using an equal gain chemical laser experiment, and by Schafer, et al. [26] and Anlauf, et al. [27], using a crossed molecular beam and a discharge flow technique, respectively. These data are compared in Table II. The data of Schafer, et al., are for back scattering only and are inconsistent with trends found for the more widely studied  $\text{F} + \text{H}_2$  reaction. Their distribution also disagrees

Table II. F + D<sub>2</sub> Pumping Distribution

Vibrational Level	E <sub>v</sub> (kcal/mole) <sup>a</sup>	k <sub>v</sub> [27]	k <sub>v</sub> [26]	k <sub>v</sub> [25]
0	0	----	0.012	----
1	8.31	0.1	0.019	----
2	16.36	0.5	0.051	0.63
3	24.15	1.0	0.285	1.0
4	31.69	0.72	1.0	<1.19
<sup>a</sup> Vibrational energy above ground state				

with the laser experiments of Basov, et al. [14]. The pumping distribution data for  $F + H_2$  includes the equal gain measurement at 539°K of Parker and Pimentel [25]; crossed molecular beam studies of Schafer, et al. [26]; discharge flow system measurements of Anlauf, et al. [27], Polanyi and Tardy [28], and Jonathan, et al. [29-31]; and the trajectory calculations of Wilkins [32]. These data are compared to those of React. (4) in Fig. 2. The abscissa in the figure  $[(E_v - E_0)/|\Delta H|]$  is the ratio of the vibrational energy of a given level to the heat released for the particular reaction. From the figure, we see that the data of Anlauf, et al., are the most consistent with the expected trends; we use this distribution and the total rate computed by Wilkins.

Reaction (4) is not sufficiently exothermic to produce  $DF(v)$  above  $v = 4$ ; however, there is some evidence in the  $H_2 + F_2$  system [6] that this reaction, running in reverse at the higher  $v$  levels, is a sink for excited species produced by reactions like (5). Hence, we use rate coefficients analogous to those of Cohen for  $H_2 + F_2$ :

$$k_{-4}(v = 5) = 4 \times 10^{12} T^{0.15} e^{30}$$

and

$$k_{-4}(v \geq 6) = 1.2 \times 10^{13} T^{0.15}$$

These values are roughly twice as large as predicted by the recent Monte Carlo calculations of Wilkins [33].

No studies have been made to determine the distribution of pumping by React. (5). Evidence that this reaction pumps to  $v = 9$  is given by the

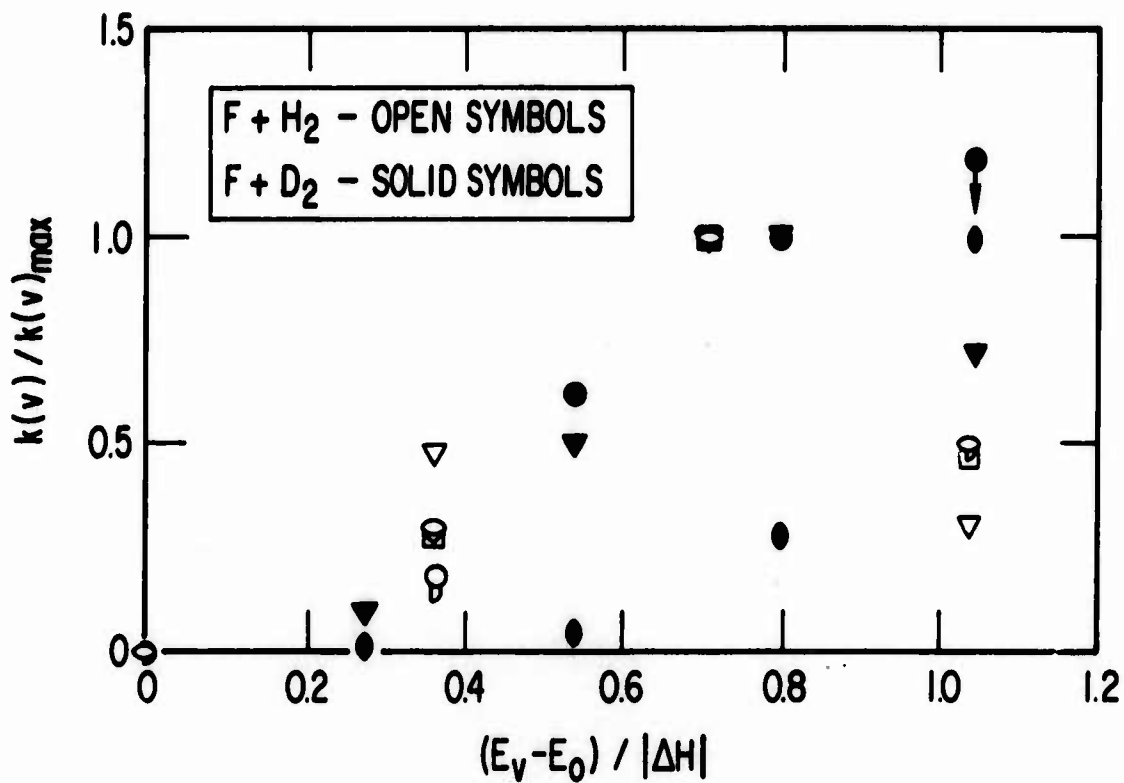


Fig. 2. Pumping distributions for  $F + H_2$  and  $F + D_2$ : equal gain technique,  $\circ$  Ref. [25]; crossed molecular beam study,  $\odot$  Ref. [26]; discharge flow system,  $\nabla$  Ref. [27];  $\square$  Ref. [28],  $\diamond$  Refs. [29] and [30],  $\circ$  Ref. [31]; Monte Carlo calculations,  $\text{D}$  Ref. [32].



spectral output of the DF laser measurements of Basov, et al. [14].

Jonathan, et al. [29, 30] have reported the distribution of pumping by  $H + F_2$ . We expect that the similarity shown in Fig. 2 between  $F + H_2$  and  $F + D_2$  will hold between  $H + F_2$  and  $D + F_2$ . In Fig. 3, we plot the distributions reported by Jonathan, et al. [29, 30]. By connecting the data points with a smooth curve and denoting the vibrational energy levels of  $DF(v)$ , we estimate the pumping distribution to be

$$k_5(0):k_5(1):k_5(2):k_5(3):k_5(4):k_5(5):k_5(6):k_5(7):k_5(8):k_5(9) \\ = 0:0.16 :0.27 :0.40 :0.57 :0.72 :0.86 : 1 :0.97 :0.61$$

With these estimates of the distribution of pumping into  $DF(v)$ , Reacts. (4) and (5) convert 79% and 46%, respectively, of the available chemical energy into vibrational energy.

### C. VIBRATIONAL-TRANSLATIONAL ENERGY TRANSFER IN DF

Vibrational deactivation of an excited species through collisions is a significant energy loss mechanism in chemical lasers,



This rate coefficient has been measured in a shock tube for  $v = 1$  by Bott and Cohen [34] over a wide temperature range for  $M = H_2, N_2, Ar$ , and  $DF$ . These measurements of the Napier time  $\rho\tau$  are converted to rate coefficients by assuming an harmonic oscillator model and using the relation

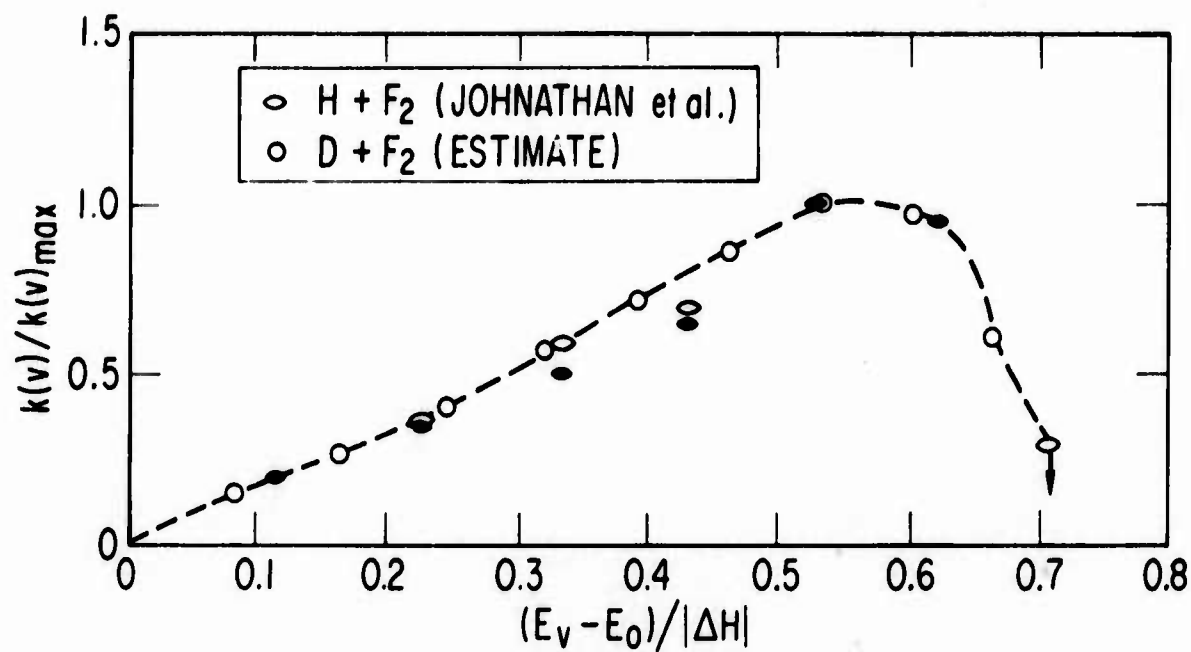


Fig. 3. Estimate of D + F<sub>2</sub> pumping distribution from H + F<sub>2</sub> data:  
 ● Ref. [29], ○ Ref. [30].

$$k = \frac{RT}{p\tau(1 - e^{-E_1/RT})} \quad (1)$$

Stephens and Cool [35] also measured the DF-DF VT rate using a chopped DF laser at 350°K. These experimental rates are shown in Fig. 4 on a Landau-Teller plot with approximate analytic rate coefficients matched to the data for the temperature range 300° to 2000°K. The character of the DF-DF rate as a function of temperature is similar to that of the HF-HF rate [6, 36]. The rate coefficients matched to the data in Fig. 4 are:

$$k_6 = 3.4 \times 10^4 T^{2.2} \quad M = H_2$$

$$k_{6a} = 4.0 \times 10^3 T^{2.2} \quad M = N_2$$

$$k_{6b} = 3.7 \times 10^{-6} T^{4.66} \quad M = Ar$$

$$k_{6c} = 4.5 \times 10^4 T^{2.2} + 5.3 \times 10^{16} T^{-2.0} \quad M = DF$$

Except for high-temperature measurements of DF-F, deactivation of DF(v) by other collision partners has not been measured. The efficiency of H<sub>2</sub> in deactivating DF is close to the efficiency of H<sub>2</sub> in deactivating HF [34]. Hence, we use the measurement of HF relaxation by D<sub>2</sub> of Bott and Cohen [36] for relaxation of DF by D<sub>2</sub>

$$k_{6d} = 0.14 T^{3.66} \quad M = D_2$$

We estimate the efficiency of F<sub>2</sub> in deactivating DF to be approximately the same as Ar, and the rate for DF-He is taken as twice the DF-Ar rate

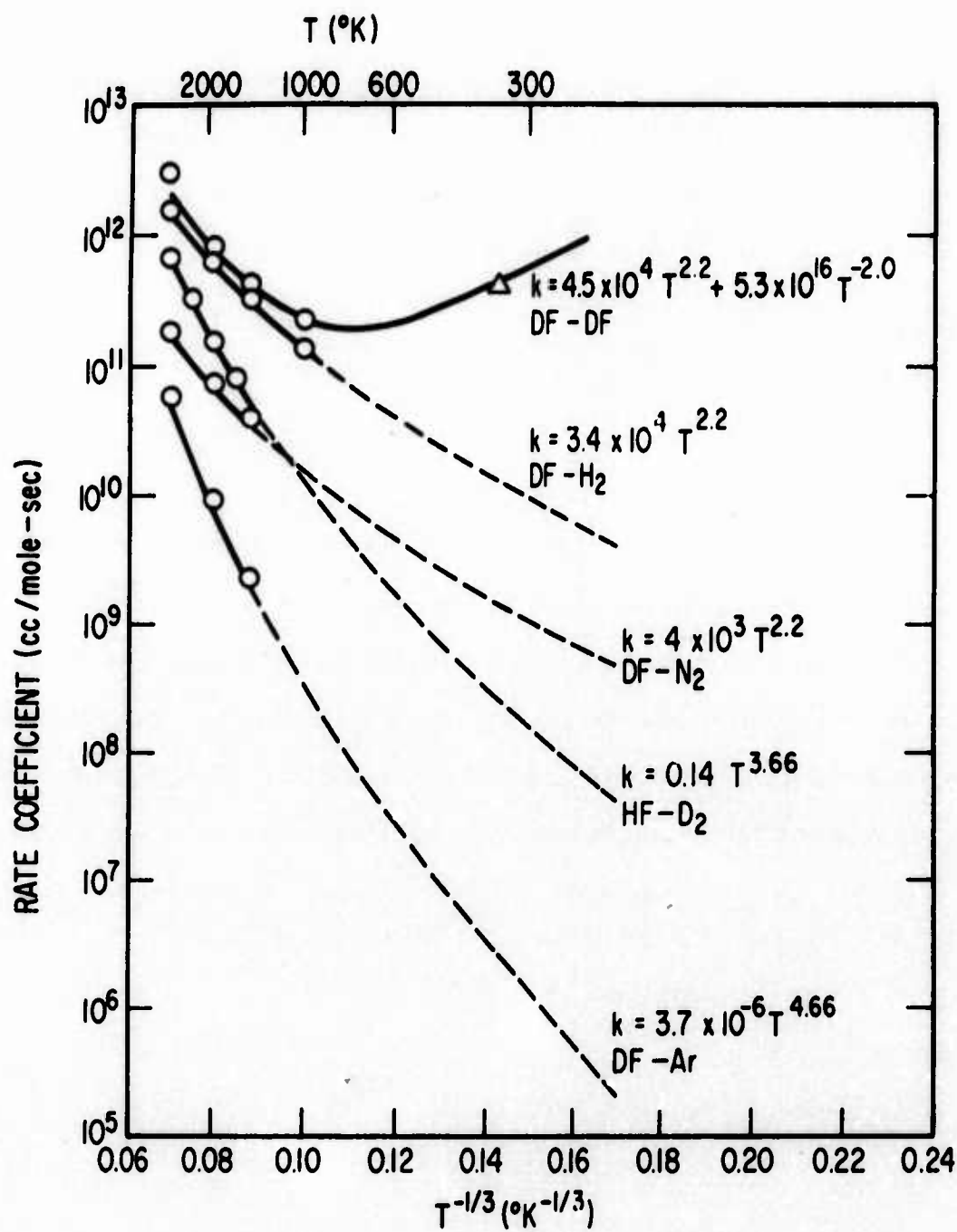


Fig. 4. Measured rate coefficients for VT deactivation of DF(1):  
 O Ref. [34],  $\Delta$  Ref. [35].

analogous to their efficiency in deactivating HF [36]. The deactivation rate for DF - CO<sub>2</sub> is assumed to be similar to that of N<sub>2</sub>. For all these reactions, we assume the deactivation rate is linear with  $v$ ; i. e., we assume an harmonic model. There has been speculation regarding the variation of these rates with  $v$ ; however, this question can only be answered by careful experiment.

We expect the deactivation rate with F and D to be quite fast. Shock tube measurements of the HF - F VT rate near 2000°K by Bott and Cohen [37] show relaxation by F to be 26.5 times more efficient than HF self-relaxation at 2000°K. Also at 2000°K, shock tube measurements of Blauer, et al. [38] show that HF-F/DF-F  $\sim$  2.4 and DF - F is approximately  $1.5 \times 10^{13}$  cc/mole-sec, which is in agreement with the shock tube measurements of Bott and Cohen [34]. Ridley and Smith [39] have measured the rate coefficients for deactivation of HCl( $v$ ) by Cl for  $v = 3, 2$ , and 1 to be  $4.8 \times 10^{12}$ ,  $1.9 \times 10^{12}$ , and  $5.8 \times 10^{11}$  cc/mole-sec at room temperature. We have used these rates to approximate the efficiency of F and D in deactivating DF( $v$ ). Thus, for M = D and F, we take

$$k_{6e}(1) = 5.0 \times 10^{12} e^{1.250}$$

$$k_{6e}(2) = 5.0 \times 10^{12} e^{0.550}$$

$$k_{6e}(v \geq 3) = 5.0 \times 10^{12}$$

The activation energies for  $v = 1$  and 2 are chosen to approximate the measurements of Ref. [39].

These values are consistent with extrapolation of Ref. [38] and with recent trajectory calculations of the HF-H VT rate by Wilkins [33] where multiple quantum deexcitation was predicted. We have deviated from the  $k_{v,v-1} = vk_{1,0}$  form for these reactions, since they are apparently chemical in nature.

#### D. VIBRATIONAL-VIBRATIONAL ENERGY TRANSFER IN DF

Since the efficiency of quantum exchange for  $\Delta v > 1$  is expected to be orders of magnitude less than for  $\Delta v = 1$ , we follow Ref. [6] and consider only



where  $v - v' = 0, 1, 2$ . Cohen includes up to  $v - v' = 3$ ; however, with the increased complexity of this system, we must limit the number of reactions. At present, no experimental data on VV transfer in DF are available. For reactions of this type, the rate varies with degree of resonance and, hence, would be expected to vary with the rotational levels of the colliding molecules. We make no attempt to correct for this effect and choose a rate suggested by Cohen [6] that is based on the theory of Rapp and Englander-Golden [40] and the data of Chen and Moore [41] for HCl

$$k_{0,1;1,0} = Z \times 4 \times 10^{-5} T \times 10^{-\Delta v/433}$$

where  $Z$  is the gas kinetic bimolecular collision rate and  $\Delta v$  is the translational energy released in wave numbers. The gas kinetic bimolecular collision rate is given by

$$Z = \left[ 8\pi RT \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2} \left( \frac{\sigma_A + \sigma_B}{2} \right)^2 N_A \quad (2)$$

and  $N_A$  is Avogadro's number. Table III contains a list of the collision diameters  $\sigma_j$  and the masses  $m_j$  used in our gas kinetic calculations. We assume that the rate coefficients behave as though the vibrational levels of the molecule are harmonic and

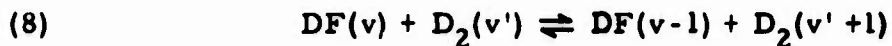
$$k_{v, v+1; v', v'-1} = (v+1)v'Z \times 4 \times 10^{-5} T \times 10^{-\Delta v/433}$$

where  $\Delta v$  is the translational energy released for each reaction.

Recent measurements [42] for HCl VV reactions indicate that this theory may not be appropriate for hydrogen halides with  $v$  and  $v' > 1$ . Although these VV rates are in question, they probably do not play a major role in predicting laser performance, as suggested by computer calculations of Kerber, Emanuel, and Whittier [43] and the analytic study by Emanuel and Whittier [44] for the HF pulsed laser.

#### E. VIBRATIONAL-VIBRATIONAL ENERGY TRANSFER BETWEEN DF AND D<sub>2</sub>

Since vibrational energy transfer between DF and D<sub>2</sub> may represent a significant loss of laser energy, we include the reaction



in our kinetic model. We use the same probability for the backward rate of this reaction as for DF-DF VV reactions,



**Table III. Molecular Parameters Used in Data Analysis**

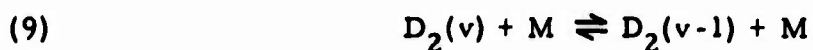
<b>Species</b>	<b>Molecular Weight</b>	<b><math>\sigma(\text{\AA})</math></b>
<b>CO<sub>2</sub></b>	<b>44.01</b>	<b>3.95</b>
<b>Ar</b>	<b>39.94</b>	<b>3.405</b>
<b>DF</b>	<b>21.01</b>	<b>3.0</b>
<b>F<sub>2</sub></b>	<b>38.00</b>	<b>3.41</b>
<b>F</b>	<b>19.00</b>	<b>2.9</b>
<b>D</b>	<b>2.02</b>	<b>2.68</b>
<b>D<sub>2</sub></b>	<b>4.03</b>	<b>2.92</b>
<b>N<sub>2</sub></b>	<b>28.01</b>	<b>3.85</b>
<b>He</b>	<b>4.00</b>	<b>2.57</b>

$$k_{-8} = (v' + 1)vZ \times 4 \times 10^{-5} T \times 10^{-\Delta v/433} \quad (3)$$

Recent measurements by Airey and Fried [45] of the rate of the HF-H<sub>2</sub> VV reaction are of the same order as predicted by Eq. (3).

F. VIBRATIONAL-TRANSLATIONAL ENERGY TRANSFER IN D<sub>2</sub>

These reactions are included to prevent unrealistic inversions in the D<sub>2</sub> populations. Hence, we include



This rate is determined from the compilation of Napier times given by Stretton in Ref. [46]. For M = Ar, this gives

$$k = 1.51 \times 10^{-5} T^{4.6}$$

We use this rate for all species except D<sub>2</sub>, D, and He. For M = D<sub>2</sub>, we increase the rate by a factor of 4.8 to be consistent with Ref. [46], and we estimate that D and He are at least twice as effective as Ar.

The proposed kinetic model for the F<sub>2</sub> + D<sub>2</sub> chemical system is summarized by Reacts. (1) - (9) of Table IV.

Table IV. Recommended Rate Coefficients for the  $D_2 - F_2 - CO_2$   
Chemical Laser

React.	Reaction <sup>a</sup>	Rate Coefficient <sup>b</sup>
1 <sup>c</sup>	$F_2 + M_1 \rightleftharpoons F + F + M_1$	$k_1 = 5.0 \times 10^{13} e^{35.3\theta}$
2	$D_2(0) + M_2 \rightleftharpoons D + D + M_2$	$k_{-2} = 10^{18} T^{-1.0}$
3 <sub>v</sub>	$DF(v) + M_1 \rightleftharpoons D + F + M_1$	$k_{3v} = 1.2 \times 10^{18} T^{-1.0} e^{(137.13 - E_v)\theta}$ $v=0, \dots, 9$
4a	$F + D_2(0) \rightleftharpoons DF(1) + D$	$k_{4a} = 2.66 \times 10^{12} e^{1.46\theta}$
4b	$F + D_2(0) \rightleftharpoons DF(2) + D$	$k_{4b} = 1.33 \times 10^{13} e^{1.46\theta}$
4c	$F + D_2(0) \rightleftharpoons DF(3) + D$	$k_{4c} = 2.66 \times 10^{13} e^{1.46\theta}$
4d	$F + D_2(0) \rightleftharpoons DF(4) + D$	$k_{4d} = 1.91 \times 10^{13} e^{1.46\theta}$
4e	$F + D_2(0) \rightleftharpoons DF(5) + D$	$k_{-4e} = 4.0 \times 10^{12} T^{0.15} e^{3\theta}$
4f <sub>v</sub>	$F + D_2(0) \rightleftharpoons DF(v) + D$	$k_{-4f_v} = 1.2 \times 10^{13} T^{0.15}$ $v=6, \dots, 9$
5a	$D + F_2 \rightleftharpoons DF(1) + F$	$k_{5a} = 5.0 \times 10^{12} e^{2.4\theta}$
5b	$D + F_2 \rightleftharpoons DF(2) + F$	$k_{5b} = 8.45 \times 10^{12} e^{2.4\theta}$
5c	$D + F_2 \rightleftharpoons DF(3) + F$	$k_{5c} = 1.25 \times 10^{13} e^{2.4\theta}$
5d	$D + F_2 \rightleftharpoons DF(4) + F$	$k_{5d} = 1.78 \times 10^{13} e^{2.4\theta}$
5e	$D + F_2 \rightleftharpoons DF(5) + F$	$k_{5e} = 2.25 \times 10^{13} e^{2.4\theta}$

Table IV. Recommended Rate Coefficients for the  $D_2 - F_2 - CO_2$   
Chemical Laser (Continued)

React.	Reaction <sup>a</sup>	Rate Coefficient <sup>b</sup>
5f	$D + F_2 \rightleftharpoons DF(6) + F$	$k_{5f} = 2.69 \times 10^{13} e^{2.4\theta}$
5g	$D + F_2 \rightleftharpoons DF(7) + F$	$k_{5g} = 3.13 \times 10^{13} e^{2.4\theta}$
5h	$D + F_2 \rightleftharpoons DF(8) + F$	$k_{5h} = 3.04 \times 10^{13} e^{2.4\theta}$
5i	$D + F_2 \rightleftharpoons DF(9) + F$	$k_{5i} = 1.91 \times 10^{13} e^{2.4\theta}$
6a <sub>v</sub>	$DF(v) + M_3 \rightleftharpoons DF(v-1) + M_3$	$k_{6a_v} = 4.0 \times 10^3 v T^{2.2}$ $v=1, \dots, 9$
6b <sub>v</sub>	$DF(v) + M_4 \rightleftharpoons DF(v-1) + M_4$	$k_{6b_v} = 3.7 \times 10^{-6} v T^{4.66}$ $v=1, \dots, 9$
6c <sub>v</sub>	$DF(v) + M_5 \rightleftharpoons DF(v-1) + M_5$	$k_{6c_v} = 4.5 \times 10^4 v T^{2.2} + 5.3 \times 10^{16} v T^{-2.0}$ $v=1, \dots, 9$
6d <sub>v</sub>	$DF(v) + M_6 \rightleftharpoons DF(v-1) + M_6$	$k_{6d_v} = 0.14 v T^{3.66}$ $v=1, \dots, 9$
6e <sub>1</sub>	$DF(1) + M_7 \rightleftharpoons DF(0) + M_7$	$k_{6e_1} = 5.0 \times 10^{12} e^{1.25\theta}$
6e <sub>2</sub>	$DF(2) + M_7 \rightleftharpoons DF(1) + M_7$	$k_{6e_2} = 5.0 \times 10^{12} e^{0.55\theta}$
6e <sub>v</sub>	$DF(v) + M_7 \rightleftharpoons DF(v-1) + M_7$	$k_{6e_v} = 5.0 \times 10^{12}$ $v=3, \dots, 9$
7a <sub>v</sub>	$DF(v) + DF(v) \rightleftharpoons DF(v-1) + DF(v+1)$	$k_{7a_v} = v(v+1) 3.06 \times 10^8 T^{1.5} 10^{-\Delta v/433}$ $v=1, \dots, 8$
7b <sub>v</sub>	$DF(v) + DF(v+1) \rightleftharpoons DF(v-1) + DF(v+2)$	$k_{7b_v} = v(v+2) 3.06 \times 10^8 T^{1.5} 10^{-\Delta v/433}$ $v=1, \dots, 7$

Table IV. Recommended Rate Coefficients for the  $D_2 - F_2 - CO_2$   
Chemical Laser (Continued)

React.	Reaction <sup>a</sup>	Rate Coefficient <sup>b</sup>
7c <sub>v</sub>	$DF(v) + DF(v+2) \rightleftharpoons DF(v-1) + DF(v+3)$	$k_{7c_v} = v(v+3) 3.06 \times 10^8 T^{1.5} 10^{-\Delta v/433} \quad v=1, \dots, 6$
8a	$DF(1) + D_2(0) \rightleftharpoons DF(0) + D_2(1)$	$k_{-8a} = 3.3 \times 10^8 T^{1.5}$
8b	$DF(2) + D_2(0) \rightleftharpoons DF(1) + D_2(1)$	$k_{-8b} = 4.05 \times 10^8 T^{1.5}$
8c	$DF(3) + D_2(0) \rightleftharpoons DF(2) + D_2(1)$	$k_{-8c} = 3.78 \times 10^8 T^{1.5}$
8d	$DF(1) + D_2(1) \rightleftharpoons DF(0) + D_2(2)$	$k_{-8d} = 1.23 \times 10^9 T^{1.5}$
8e	$DF(2) + D_2(1) \rightleftharpoons DF(1) + D_2(2)$	$k_{-8e} = 1.51 \times 10^9 T^{1.5}$
9 <sub>v</sub>	$D_2(v) + M_8 \rightleftharpoons D_2(v-1) + M_8$	$k_{9_v} = 1.51 \times 10^{-5} v T^{4.6}$
10 <sub>v</sub> <sup>d</sup>	$DF(v) + CO_2(00^0_0) \rightleftharpoons DF(v-1) + CO_2(00^0_1)$	$k_{10_v} = 4.7 \times 10^{17} T^{-2} \quad v=1, \dots, 9$
11	$CO_2(00^0_1) + CO_2(00^0_0) \rightleftharpoons CO_2(10^0_0) + CO_2(01^1_0)$	$k_{11} = 3.4 \times 10^1 T^{2.5} e^{0.39\theta}$
12 <sup>0</sup>	$CO_2(00^0_1) + CO_2(00^0_0) \rightleftharpoons CO_2(02^0_0) + CO_2(01^1_0)$	$k_{12}^0 = 1.2 \times 10^1 T^{2.5} e^{\theta}$
13	$CO_2(11^1_0) + CO_2(00^0_0) \rightleftharpoons CO_2(10^0_0) + CO_2(01^1_0)$	$k_{13} = 7.5 \times 10^{10} T^{0.5}$
14	$CO_2(030) + CO_2(00^0_0) \rightleftharpoons CO_2(10^0_0) + CO_2(01^1_0)$	$k_{14} = 1.1 \times 10^9 T^{0.5}$
15 <sup>0</sup>	$CO_2(030) + CO_2(00^0_0) \rightleftharpoons CO_2(02^0_0) + CO_2(01^1_0)$	$k_{15}^0 = 1.1 \times 10^{11} T^{0.5}$
15 <sup>2</sup>	$CO_2(030) + CO_2(00^0_0) \rightleftharpoons CO_2(02^2_0) + CO_2(01^1_0)$	$k_{15}^2 = 2.25 \times 10^{11} T^{0.5}$

Table IV. Recommended Rate Coefficients for the  $D_2 - F_2 - CO_2$   
Chemical Laser (Continued)

React.	Reaction <sup>a</sup>	Rate Coefficient <sup>b</sup>
16	$CO_2(10^0 0) + CO_2(00^0 0) \rightleftharpoons CO_2(01^1 0) + CO_2(01^1 0)$	$k_{16} = 1.5 \times 10^{11} T^{0.5}$
17 <sup>0</sup>	$CO_2(02^0 0) + CO_2(00^0 0) \rightleftharpoons CO_2(01^1 0) + CO_2(01^1 0)$	$k_{17}^0 = 1.5 \times 10^{11} T^{0.5}$
17 <sup>2</sup>	$CO_2(02^2 0) + CO_2(00^0 0) \rightleftharpoons CO_2(01^1 0) + CO_2(01^1 0)$	$k_{17}^2 = 1.2 \times 10^{12} T^{0.5}$
18a	$CO_2(00^0 1) + M_3 \rightleftharpoons CO_2(11^1 0) + M_3$	$k_{18a} = 8.85 \times 10^{-4} T^{-1.75} e^{-1.4840}$
18b	$CO_2(00^0 1) + M_9 \rightleftharpoons CO_2(11^1 0) + M_9$	$k_{18b} = 1.13 \times 10^{-7} T^{5.8} e^{-2.4360}$
18c	$CO_2(00^0 1) + M_{10} \rightleftharpoons CO_2(11^1 0) + M_{10}$	$k_{18c} = 1.2 \times 10^6 T^{1.5}$
19a	$CO_2(00^0 1) + M_3 \rightleftharpoons CO_2(030) + M_3$	$k_{19a} = 6.8 \times 10^{-7} T^{5.55} e^{-1.4840}$
19b	$CO_2(00^0 1) + M_9 \rightleftharpoons CO_2(030) + M_9$	$k_{19b} = 8.7 \times 10^{-11} T^{6.6} e^{-2.4360}$
19c	$CO_2(00^0 1) + M_{10} \rightleftharpoons CO_2(030) + M_{10}$	$k_{19c} = 9.2 \times 10^2 T^{2.3}$
20	$CO_2(11^1 0) + M_{11} \rightleftharpoons CO_2(030) + M_{11}$	$k_{20} = 2.6 \times 10^7 T^{1.5}$
21 <sup>0</sup>	$CO_2(11^1 0) + M_{11} \rightleftharpoons CO_2(02^0 0) + M_{11}$	$k_{21}^0 = 8.6 \times 10^{-3} T^{-4.19} e^{0.9030}$
21 <sup>2</sup>	$CO_2(11^1 0) + M_{11} \rightleftharpoons CO_2(02^2 0) + M_{11}$	$k_{21}^2 = 7.9 \times 10^4 T^{2.5} e^{4.410}$
22	$CO_2(11^1 0) + M_{11} \rightleftharpoons CO_2(10^0 0) + M_{11}$	$k_{22} = 5.9 T^{3.78} e^{0.5490}$
23 <sup>0</sup>	$CO_2(030) + M_{11} \rightleftharpoons CO_2(02^0 0) + M_{11}$	$k_{23}^0 = 3.87 \times 10^2 T^{3.3} e^{1.240}$

Table IV. Recommended Rate Coefficients for the  $D_2 - F_2 - CO_2$   
Chemical Laser (Continued)

React.	Reaction <sup>a</sup>	Rate Coefficient <sup>b</sup>
23 <sup>2</sup>	$CO_2(030) + M_{11} \rightleftharpoons CO_2(02^2 0) + M_{11}$	$k_{23}^2 = 5.7 \times 10^2 T^{3.32} e^{-1.220}$
24	$CO_2(030) + M_{11} \rightleftharpoons CO_2(10^0 0) + M_{11}$	$k_{24} = 4.9 \times 10^2 T^{3.04} e^{-1.060}$
25 <sup>c</sup>	$CO_2(10^0 0) + M_{11} \rightleftharpoons CO_2(02^0 0) + M_{11}$	$k_{25}^0 = 2.6 \times 10^8 T^{1.5}$
25 <sup>2</sup>	$CO_2(10^0 0) + M_{11} \rightleftharpoons CO_2(02^2 0) + M_{11}$	$k_{25}^2 = 5.8 \times 10^8 T^{1.5}$
26a	$CO_2(10^0 0) + M_{12} \rightleftharpoons CO_2(01^1 0) + M_{12}$	$k_{26a} = 4.4 \times 10^2 T^{3.26} e^{-1.480}$
26b	$CO_2(10^0 0) + M_{13} \rightleftharpoons CO_2(01^1 0) + M_{13}$	$k_{26b} = 1.5 \times 10^3 T^{2.95} e^{-0.84330}$
26c	$CO_2(10^0 0) + M_{14} \rightleftharpoons CO_2(01^1 0) + M_{14}$	$k_{26c} = 1.65 \times 10^{14} T^{-1.0}$
27	$CO_2(02^2 0) + M_{11} \rightleftharpoons CO_2(02^0 0) + M_{11}$	$k_{27} = 5.9 \times 10^8 T^{1.5}$
28a <sup>0</sup>	$CO_2(02^0 0) + M_{12} \rightleftharpoons CO_2(01^1 0) + M_{12}$	$k_{28a}^0 = 2.4 \times 10^3 T^{3.1} e^{-1.40}$
28b <sup>0</sup>	$CO_2(02^0 0) + M_{13} \rightleftharpoons CO_2(01^1 0) + M_{13}$	$k_{28b}^0 = 2.8 \times 10^{13} T^{2.95} e^{-0.84330}$
28c <sup>0</sup>	$CO_2(02^0 0) + M_{14} \rightleftharpoons CO_2(01^1 0) + M_{14}$	$k_{28c}^0 = 3.13 \times 10^{14} T^{-1.0}$
28a <sup>2</sup>	$CO_2(02^2 0) + M_{12} \rightleftharpoons CO_2(01^1 0) + M_{12}$	$k_{28a}^2 = 6.0 \times 10^2 T^{3.31} e^{-1.30}$
28b <sup>2</sup>	$CO_2(02^2 0) + M_{13} \rightleftharpoons CO_2(01^1 0) + M_{13}$	$k_{28b}^2 = 3.3 \times 10^3 T^{2.95} e^{-0.84330}$
28c <sup>2</sup>	$CO_2(02^2 0) + M_{14} \rightleftharpoons CO_2(01^1 0) + M_{14}$	$k_{28c}^2 = 3.68 \times 10^{14} T^{-1.0}$



Table IV. Recommended Rate Coefficients for the  $D_2 - F_2 - CO_2$   
Chemical Laser (Continued)

React.	Reaction <sup>a</sup>	Rate Coefficient <sup>b</sup>
29a	$CO_2(01^1_0) + M_{12} \rightleftharpoons CO_2(00^0_0) + M_{12}$	$k_{29a} = 2.17 \times 10^{-2} T^{-4.19} e^{-1.132\theta}$
29b	$CO_2(01^1_0) + M_{13} \rightleftharpoons CO_2(00^0_0) + M_{13}$	$k_{29b} = 8.27 \times 10^2 T^{2.95} e^{-0.8433\theta}$
29c	$CO_2(01^1_0) + M_{14} \rightleftharpoons CO_2(00^0_0) + M_{14}$	$k_{29c} = 9.2 \times 10^{13} T^{-1.0}$
<sup>a</sup> Catalytic species: $M_1 = \text{all species}$ $M_2 = 1.75D_2, 20D, F, Ar, He, DF, F_2, CO_2$ $M_3 = CO_2$ $M_4 = Ar, 2He, F_2$ $M_5 = DF$ $M_6 = D_2$ $M_7 = F, D$ $M_8 = 4.8D_2, 2D, F, Ar, 2He, DF, F_2, CO_2$ $M_9 = He, Ar, 4D, 2F_2$ $M_{10} = D_2, 53DF, 53F$ $M_{11} = CO_2, F, DF, 2D_2, Ar, 1.5He, 2D, F_2$ $M_{12} = CO_2, F_2, F, DF, 0.06Ar$ $M_{13} = He$ $M_{14} = D_2, D$		

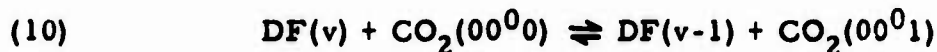
<sup>b</sup>The rate coefficients  $k_f$  and  $k_b$  designate forward and backward rates, respectively, with units in terms of moles,  $cm^3$ , and sec. For each reaction, the missing rate coefficient is determined from the equilibrium constant.

<sup>c</sup>The quantity  $\theta = -(10^3/RT)$ , where the temperature  $T$  is in  $^{\circ}K$  and  $R$  is 1.987 cal/mole  $^{\circ}K$ .

<sup>d</sup>This temperature dependence may be too pronounced (see Section III).

### III. DF - CO<sub>2</sub> VIBRATIONAL ENERGY TRANSFER

The most important reaction in the DF-CO<sub>2</sub> laser system is the transfer of vibrational energy from DF(v) to CO<sub>2</sub>(00<sup>0</sup>1)



The rate coefficient of this reaction has been determined to be  $3.82 \times 10^{12}$  cc/mole-sec for  $v = 1$  by Stephens and Cool [35] using a laser-induced fluorescence technique at 350°K. Preliminary measurements of Cool [47] at 300°K suggest that this rate coefficient may vary as strongly as  $T^{-2}$ . Basov, et al. [14] estimate this rate to be  $9 \times 10^{11}$  cc/mole-sec at 300°K from a DF-CO<sub>2</sub> pulsed laser experiment. The rate of vibrational energy transfer from other hydrogen halides to CO<sub>2</sub> has also been measured by the laser fluorescence technique. Stephens and Cool [35] found  $k_{\text{HF-CO}_2} = 8.1 \times 10^{11}$  cc/mole-sec at 350°K, and Chen, et al. [48] report  $k_{\text{HCl-CO}_2} = 1.8 \times 10^{12}$  cc/mole-sec and  $k_{\text{HI-CO}_2} = 2.4 \times 10^{12}$  cc/mole-sec. Although the degree of resonance for  $v = 1$  is 1612 cm<sup>-1</sup>, 537 cm<sup>-1</sup>, and -116 cm<sup>-1</sup>, respectively, for these reactions compared to 558 cm<sup>-1</sup> for DF, their efficiencies of transfer are all the same order of magnitude as the DF-CO<sub>2</sub> value.

An analysis of the energy spacing of the  $\Delta v = 1$  transitions in DF (Fig. 1) shows that the closest resonance for  $J = 0$  is at  $v = 8$ . We have also calculated the relative probabilities of transfer as a function of  $v$ , by assuming rotational equilibrium in DF(v) and CO<sub>2</sub>(00<sup>0</sup>0) at the translation temperature. We assume that the transfer probability decreases about one order of

magnitude for every  $150 \text{ cm}^{-1}$  of energy separation as Callear [49] found for certain diatomics. In the final states, all values of  $J$  are assumed possible; however, because of the resonance argument, those values that release the smallest quantity of energy to translation are most likely. At  $300^\circ\text{K}$ , the higher levels,  $v = 6, 7$ , and  $8$ , are still most likely to transfer. A calculation made on the assumption of a decrease of one order of magnitude for every  $450 \text{ cm}^{-1}$  of energy separation gave a similar result. At this time, a rate of transfer based on these resonance and equilibrium population arguments seems unwarranted, especially in light of the apparent insensitivity to resonance exhibited by the transfer efficiencies of other hydrogen halides. Hence, until more data are available, we estimate the rate to be the same for all  $v$ .

We use the values of Refs. [35] and [47] to obtain

$$k_{10_v} = 4.7 \times 10^{17} T^{-2}$$

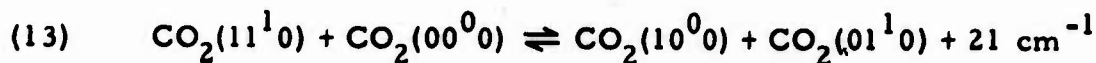
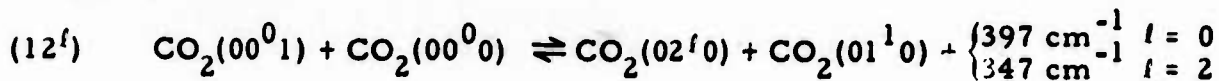
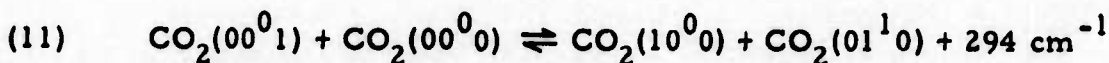
Since the temperatures used to determine this function are very close together, this rate coefficient should be used with prudence outside the  $300^\circ$  to  $350^\circ\text{K}$  temperature range. In fact, for large temperature variations the  $3.82 \times 10^{12} \text{ cc/mole-sec}$  rate of Ref. [35] may be more appropriate.

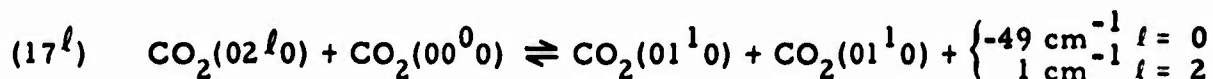
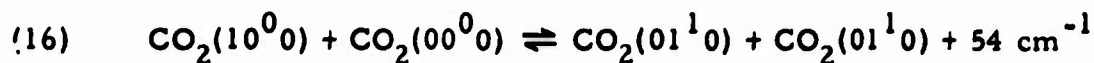
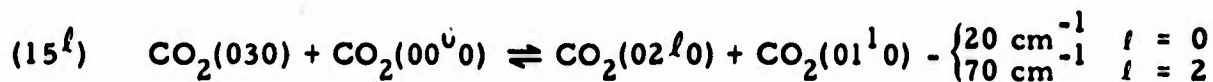
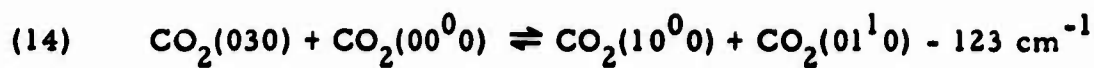
#### IV. CO<sub>2</sub> KINETICS

An extensive theoretical study of the rates of VV and VT reactions of CO<sub>2</sub>-CO<sub>2</sub> and CO<sub>2</sub>-N<sub>2</sub> has been made by Herzfeld [50, 51]. We use his work as the basis for selecting the reactions shown in Fig. 1, and we use Ref. [51] as a guide for estimating rates when experimental measurements are not available. In addition, many of the reactions in our model are common to those reviewed by Taylor and Bitterman [5]. The states (03<sup>1</sup>0) and (03<sup>3</sup>0) are assumed in equilibrium and statistically combined. We denote this combined state as (030) and adjust the kinetics accordingly. The small energy difference, 73 cm<sup>-1</sup>, between these states is neglected, and both states are assigned the energy of (03<sup>1</sup>0).

##### A. VIBRATIONAL - VIBRATIONAL TRANSFER IN CO<sub>2</sub>

Intermolecular VV transfer processes represent important and fast mechanisms for energy transfer within CO<sub>2</sub>. These reactions have a significant effect on the relative populations of the CO<sub>2</sub> levels, including those that participate in lasing.





Rate coefficients for Reacts. (11) and (12) have been calculated by Herzfeld [51] between 300° and 3000°K. We have approximated these rates as a function of T to be

$$k_{11} = 34.0 T^{2.5} e^{0.39\theta}$$

$$k_{12}^l = \begin{cases} 12.0 T^{2.5} e^{\theta} & l = 0 \\ \text{neglected} & l = 2 \end{cases}$$

The value of  $k_{12}^2$  is nearly two orders of magnitude less than  $k_{12}^0$  [51].

Theoretical or experimental estimates of rates of Reacts. (13) - (15) are not available. There is, however, a laser fluorescence measurement by Rhodes, Kelly, and Javan [52] that has been interpreted as either the rate of React. (16) or (17). At 296°K, they found this rate coefficient to be  $7.5 \times 10^{12}$  cc/mole-sec. Sharma [53], using the theory of Sharma and Brau [54, 55], and Seeber [56], using a modified SSH theory, have calculated the rate coefficient of React. (16) at 300°K and find  $3.2 \times 10^{12}$  and  $2.5 \times 10^{12}$  cc/mole-sec, respectively.

Sharma [53] suggests that the experiment of Rhodes, et al. [52] is controlled by React. (17<sup>2</sup>), which he finds is 21 times faster than React. (16). Seeber [56] rejects this interpretation and suggests that the measurement reflects a stimulated Raman effect, multiple photon process, and a subsequent rotational relaxation. Even if this interpretation is correct, this effect is enhanced by the simultaneous application of 10.6 and 9.6- $\mu$ m radiation in the experiment of Ref. [52] and would not arise during normal lasing conditions. Nevertheless, interpretation of the experiment remains in question. Seeber [56] calculates  $k_{17}^2 \approx 8k_{16}$ , and Seeber and Sharma both find  $k_{17}^2$  to be larger than  $k_{17}^0$  by the factors of 8 and 35, respectively.

Other measurements of the relaxation of the (10<sup>0</sup>0) state [57 - 62] give rate coefficients ranging from 0.4 to  $2.8 \times 10^{11}$  cc/mole-sec. Interpretation of these measurements is very difficult, and the uncertainty in the reported rate coefficients is large.

In view of these uncertainties, we estimate the rates of Reacts. (16) and (17<sup>1</sup>) from the SSH calculations of Seeber [56] and assume that the probability is independent of T; hence, we set

$$k_{16} = 1.5 \times 10^{11} T^{0.5}$$

$$k_{17}^0 = 1.5 \times 10^{11} T^{0.5}$$

$$k_{17}^2 = 1.2 \times 10^{12} T^{0.5}$$

Reaction (13) is similar to React. (17<sup>1</sup>), in that both involve the transfer of one quantum of  $\nu_2$  to a ground state molecule; hence, we set<sup>1</sup>

$$k_{13} = 0.5 k_{17}^0$$

Approximation of the bending mode of CO<sub>2</sub> by an harmonic oscillator model suggests that<sup>1</sup>

$$k_{15}^0 = 0.75 k_{17}^0$$

$$k_{15}^2 = 1.5 k_{17}^0$$

Reaction (14) involves the transfer of one  $\nu_2$  quantum and the excitation of  $\nu_1$  at the expense of  $2\nu_2$ . We estimate that this process is  $10^{-2}$  times as efficient as React. (15), i. e., one order of magnitude slower for each quantum changing modes; hence, we set

$$k_{14} = 10^{-2} k_{15}^0$$

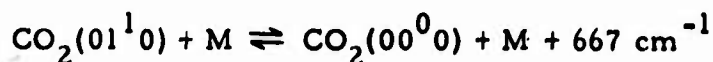
#### B. VIBRATIONAL - TRANSLATIONAL TRANSFER

We discuss two types of reactions in this section. The first type is the VT process by which exactly one quantum of an excited mode is

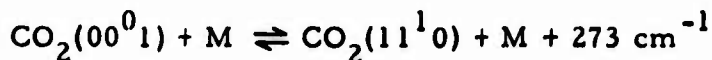
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<sup>1</sup>The value of  $k_{17}^0$  is used as a reference, since the degree of resonance is much less than that of (17<sup>2</sup>) for these reactions.

exchanged for translational energy during a collision. An example of such a reaction is



The second reaction type is an intramolecular VV process that leaves the excited molecule in a different mode from the original state. These processes differ from the intermolecular VV reactions where the state of both molecules is changed during the collision. Again, the excess energy is exchanged for translational energy. An example of such a reaction is



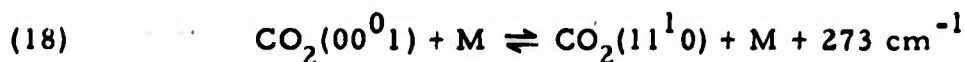
Both processes represent transfer of vibrational energy to translational energy of the colliding pair.

Deactivation of the upper laser level by collisions represents a loss of laser energy, whereas deactivation of the lower laser level enhances the inversion. In addition, mechanisms that couple levels adjacent to and below the lasing levels are important for realistic computer modeling. In Table IV, Reacts.(18) - (29) include processes of this type considered important in the modeling of  $\text{CO}_2$  relaxation for transfer laser simulation. We first discuss those reactions where experimental measurements are available, and then we complete the discussion by making theoretical estimates of the rates of the remaining reactions.



## 1. DEACTIVATION OF THE UPPER LASER LEVEL

Reactions (18) and (19) represent a loss of laser power through collisional deexcitation of  $\text{CO}_2(00^0_1)$



Experimental data for the relaxation rate of  $\text{CO}_2(00^0_1)$  are generally presented without specifying the final state of  $\text{CO}_2$ . The most probable final states are those of Reacts. (18) and (19). One might also expect  $\text{CO}_2(04^1_0)$  to be a product of this VT reaction of  $\text{CO}_2(00^0_1)$ ; however, we have limited our consideration to levels below  $(00^0_1)$ . Herzfeld's calculations show that the final state  $(03^3_0)$  may be neglected, while the ratio for pure  $\text{CO}_2$  of  $k_{19}$  (with final state  $(03^1_0)$ ) to  $k_{18}$  may be approximated by  $7.7 \times 10^{-4} T^{0.8}$ . This ratio is 0.074 at 300°K and 0.19 at 1000°K; hence, React. (18) is expected to be the dominant mechanism over this temperature range.

Experimental measurements of the relaxation of mode  $\nu_3$  in  $\text{CO}_2$  have been made by several techniques. Laser fluorescence measurements have been made by several investigators. Hocker, et al. [63] found this rate to be  $385 \text{ torr}^{-1} \text{-sec}^{-1}$  for pure  $\text{CO}_2$  at room temperature. Similar measurements were made at 293°K for the relaxation of  $\nu_3$  by collisions with He,  $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , and pure  $\text{CO}_2$  by Moore, et al. [64] and by Yardley and Moore [65] for collisions with He, Ne, Ar, Kr, Xe, and pure  $\text{CO}_2$ . Alexander, et al. [66] measured the relaxation rate in pure  $\text{CO}_2$  at 233° and 293°K. A comprehensive

study of the temperature variation of this relaxation rate in pure  $\text{CO}_2$  and  $\text{N}_2$  has been made by Rosser, Wood, and Gerry [67]. Rosser and Gerry [68, 69] have also measured this rate over a wide temperature range for deactivation by He,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , NO, and  $\text{Cl}_2$ . The temperature dependence of  $\nu_3$  relaxation for deactivation by  $\text{H}_2$ , He, Ne, Ar, Kr, Xe, HD, and  $\text{D}_2$  over the range  $298^\circ$  to  $800^\circ\text{K}$  is given by Stephenson, Wood, and Moore [70]. Deactivation of  $\nu_3$  by DF and HF has been measured by Chang, McFarlane, and Wolga [71] at  $348^\circ$  and  $373^\circ\text{K}$  and by Stephens and Cool [35] at  $350^\circ\text{K}$ . With the use of a standard modulated light source, instead of a laser, Houghton [72] measured the relaxation of  $\nu_3$  in pure  $\text{CO}_2$  and in Ar. Cheo [61, 62] measured this relaxation rate at  $300^\circ\text{K}$  for pure  $\text{CO}_2$ ,  $\text{H}_2$ , He,  $\text{N}_2$ , and other species with the pulse-gain method. The shock tube has also been used to study this relaxation rate by Simpson and Chandler [73] for mixtures of pure  $\text{CO}_2$  and  $\text{CO}_2$  with Ar,  $\text{N}_2$ , Ne, He,  $\text{D}_2$ , and  $\text{H}_2$  over a wide temperature range. In general, their results are in poor agreement with laser fluorescence measurements. We expect that the process involved in relaxation of  $\nu_3$  in the shock tube is much more complex than that in the laser fluorescence measurements, since with laser excitation only one state ( $00^0_1$ ) is produced in abundance and interpretation of the intramolecular VV data is more straightforward. The relaxation times observed with laser fluorescence are essentially a direct measure of ( $00^0_1$ ) deactivation, to ( $11^1_0$ ) based on the calculation of Herzfeld [51], whereas, in the shock tube, many adjacent levels are contributing to the activation and deactivation of  $\nu_3$  and the interpretation of  $\rho\tau$  is much more complicated. We expect that detailed modeling of the  $\text{CO}_2$  kinetics may be

helpful in explaining these shock tube results. Similar problems have been found for measurements made with the spectrophone technique [74 - 79]. Levinson, et al. [80] have measured the relaxation rate of  $\text{CO}_2(00^01)$  by exciting a gas mixture with a current pulse and monitoring the 4.3- $\mu\text{m}$  spontaneous decay. Finally, Biryukov, Serikov, and Trekhov [81] measured the rate of relaxation of  $\nu_3$  induced by collisions with  $\text{N}_2$ , He, and  $\text{H}_2\text{O}$  and in pure  $\text{CO}_2$  with the phase method.

Reduction of the experimental relaxation times to rate coefficients is not always a straightforward process. Taylor and Bitterman [5] have used the 5-reaction model of Taylor, et al. [82] to reduce the  $p\tau$  data for  $(00^01)$ . We believe that it is just as appropriate to interpret the laser fluorescence measurements when intermolecular VV processes are not involved as direct measurements of  $k_{18}$ . Hence, we use

$$k_{18} = \frac{RT}{P\tau_{\text{CO}_2-M}} \quad (4)$$

to reduce this data. The ratio of  $k_{19}$  to  $k_{18}$  calculated by Herzfeld is then used to determine  $k_{19}$ .

Reduction of the shock tube data of Ref. [73] represents an even more difficult problem. We have not used these data, since they are in poor agreement with other measurements. In Fig. 5, we show the rate coefficients for the various species of interest in our model. For modeling simplicity, rates for all species have been approximated by one of three different functions.

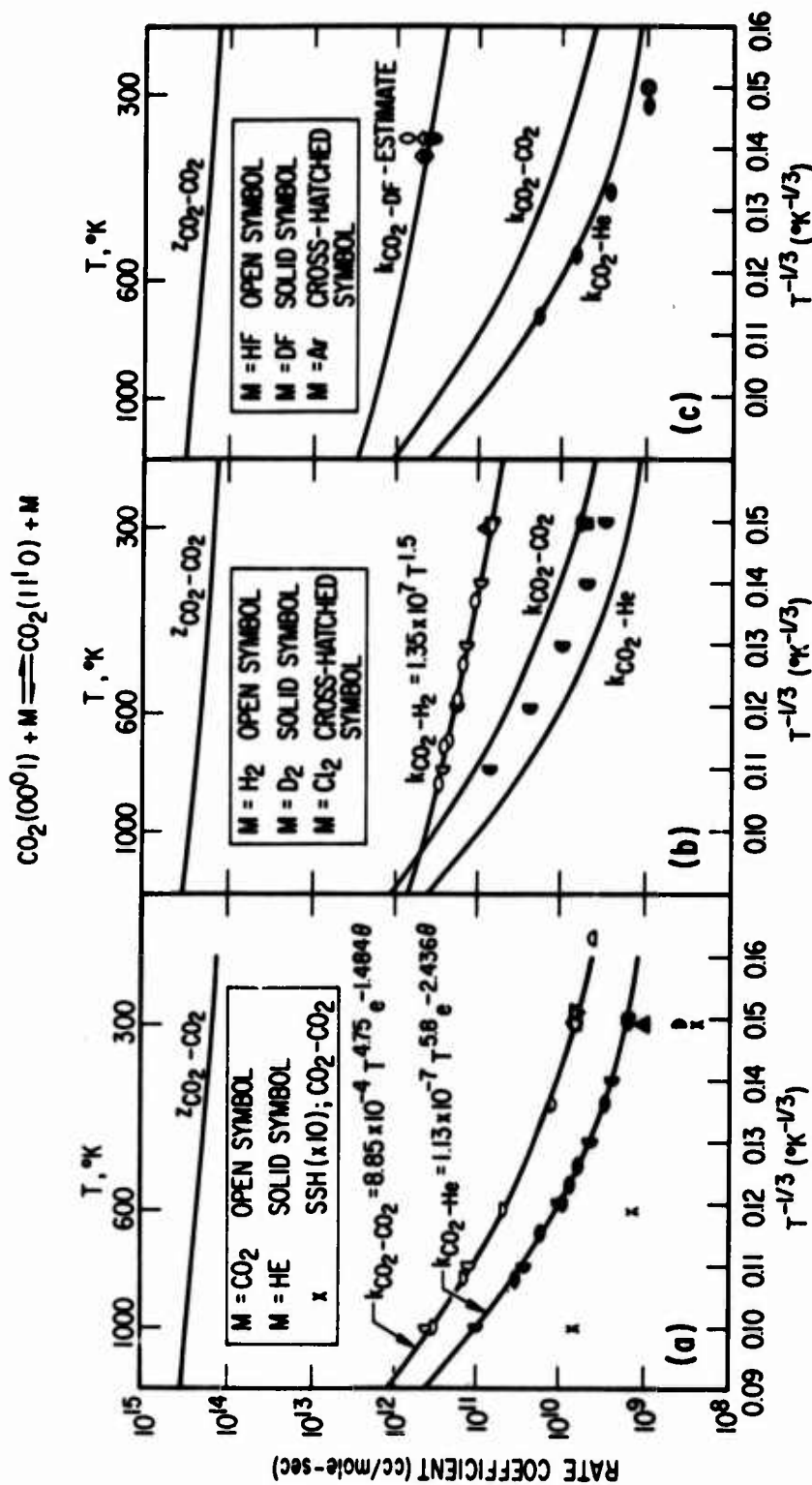


Fig. 5. Experimentally derived rate coefficients for deactivation of  $\text{CO}_2(00^0_1)$  by M: x SSH calculations, Ref. [51]; laser fluorescence,  $\circ$  Ref. [35],  $\triangle$  Ref. [63],  $\square$  Ref. [64],  $\diamond$  Ref. [65],  $\nabla$  Ref. [66],  $\nabla$  Ref. [67],  $\nabla$  Ref. [68], and [69],  $\circ$  Ref. [70],  $\diamond$  Ref. [71]; pulse gain,  $\Delta$  Refs. [61] and [62]; other fluorescence,  $\nabla$  Ref. [72],  $\nabla$  Ref. [80]; phase method,  $\triangle$  Ref. [81]. (a) Deactivation by  $\text{CO}_2$  and He. (b) Deactivation by  $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{Cl}_2$ . (c) Deactivation by Ar, HF, and DF.

For  $\text{CO}_2\text{-CO}_2$ , we have approximated the data of Rosser, et al. [67] and Rosser and Gerry [69] to be

$$k_{18a} = 8.85 \times 10^{-4} T^{4.75} e^{-1.4840}$$

and for  $\text{CO}_2\text{-He}$ , we find that

$$k_{18b} = 1.13 \times 10^{-7} T^{5.8} e^{-2.4360}$$

approximates the data of Rosser and Gerry [68] and Stephenson, et al. [70]. For  $M = \text{H}_2$  (Fig. 5b), we find that a  $T^{1.5}$  temperature dependence matches the data of Refs. [69] and [70]. Hence, from Refs. [64] and [70], we estimate the rate coefficient for deactivation by  $\text{D}_2$  to be

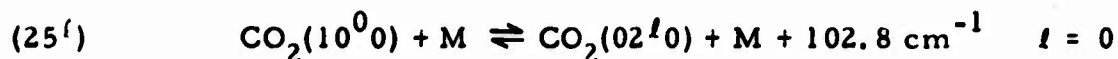
$$k_{18c} = 1.2 \times 10^6 T^{1.5}$$

In addition, we estimate from Refs. [35] and [71] that DF is 4.5 times as effective as  $\text{H}_2$  at 350° K in deactivating  $\nu_3$ . We feel that the large  $\text{CO}_2\text{-DF}$  deactivation rate at 350° K indicates a weak temperature dependence such as  $T^{1.5}$ . Relaxation of  $\nu_3$  by Ar is approximately as fast as He [70]. We also use four times the  $\text{CO}_2\text{-He}$  rate for D by assuming  $\text{CO}_2\text{-D}_2$  and  $\text{CO}_2\text{-D}$  are about the same at room temperature, and we estimate the rate of deactivation by F to be similar to DF. We assume that the rate coefficient for  $\text{F}_2$  is similar to  $\text{Cl}_2$ ; hence, we take  $\text{CO}_2\text{-F}_2$  rate to be twice that for  $\text{CO}_2\text{-He}$ . In Fig. 5a, the SSH

rate for  $\text{CO}_2\text{-CO}_2$  calculated by Herzfeld has been increased by a factor of 10 for graphic comparison with experimental data.

## 2. TRANSFER BETWEEN FERMI RESONANCE STATES

Theoretical SSH calculations by Herzfeld [51] and Seeber [56] for pure  $\text{CO}_2$  indicate that the rate of energy transfer between the strongly coupled levels in Fermi resonance



is fast. However, these calculations also show that the reaction coupling the levels not in Fermi resonance,  $(25^2)$ , is faster than  $(25^0)$ . The laser fluorescence measurement of Rhodes, Kelly, and Javan [52] at 300°K in pure  $\text{CO}_2$  indicates that  $k_{25}^0$  or  $k_{25}^2$  is possibly 10 times faster than the calculated rate coefficients of Ref. [51], which vary as  $T^{1.5}$ . Since interpretation of this experiment remains in question, we use the results of Seeber at 300°K, and the rate coefficients are assumed proportional to  $T^{1.5}$ ,

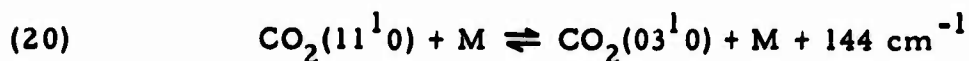
$$k_{25}^0 = 2.6 \times 10^8 T^{1.5}$$

$$k_{25}^2 = 5.8 \times 10^8 T^{1.5}$$

Herzfeld's calculations also show that  $\text{N}_2$  is nearly as efficient as  $\text{CO}_2$  for these reactions. We adjust the rate coefficient for each species such that all have nearly the same probability per collision as  $\text{CO}_2$ . Note the rate of

React. (25<sup>1</sup>) during lasing will always be less than the transfer rate of DF to CO<sub>2</sub>.

The transfer between the other states in Fermi resonance, (11<sup>1</sup>0, 03<sup>1</sup>0), is given in React. (20):



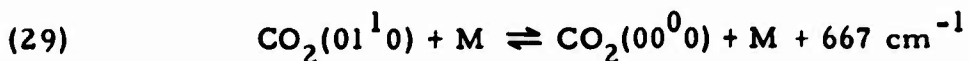
Although Herzfeld does not compute this rate, he does compute the total rate of deactivation of the combined (11<sup>1</sup>0, 03<sup>1</sup>0) state to be 20 times slower than React. (25<sup>0</sup>) at 300° K. This is probably a lower limit on k<sub>20</sub>; we estimate

$$k_{20} \approx k_{25}^0 / 10$$

In our model, React. (20) includes the relaxation between the levels (11<sup>1</sup>0) and (03<sup>3</sup>0) that are not in Fermi resonance. In any case, React. (20) is of very little importance during lasing.

### 3. DEACTIVATION OF THE BENDING MODE OF CO<sub>2</sub>

Relaxation of mode ν<sub>2</sub> of CO<sub>2</sub> has been widely studied [83 - 86]. Taylor and Bitterman [5] have compiled relaxation rates for this reaction



and they indicate a "best fit" over the temperature range of interest for M = CO<sub>2</sub>, He, H<sub>2</sub> and for other species not of interest in our model.

Conversion of the recommendations of Ref. [5] to forward rate coefficients with Eq. (1) yields for  $M = \text{CO}_2$

$$k_{29a} = 2.17 \times 10^{-2} T^{4.19} e^{-1.1320}$$

For He, we use

$$k_{29b} = 8.27 \times 10^{-2} T^{2.95} e^{-0.84330}$$

The recommended value for  $M = \text{H}_2$  decreases with  $T$ . Sharma [85], using the theory of Sharma and Brau [54, 55], has found the efficiency of  $\text{H}_2$  in deactivating  $\nu_2$  to vary approximately as  $T^{-1}$ , and the agreement of theory and experiment is good. Thus, for  $M = \text{D}_2$ , we assume the rate is proportional to  $T^{-1}$  and adjust it to the value reported by Cottrell and Day [86] at 303°K, since their values for  $M = \text{CO}_2$  and He are close to the "best fit" curves of Ref. [5]. In addition, Simpson and Chandler [73] have determined this rate from their shock tube measurements. Although these values are in closer agreement with other measurements than their observed relaxation curves for  $(00^01)$ , we have not used their values in the present model. The temperature variation of these rate coefficients is shown in Fig. 6, along with values calculated by Herzfeld [51] for pure  $\text{CO}_2$ . The overall agreement of the theoretical and experimental rates is much better than that found for relaxation of  $\nu_3$ .

Relaxation times for  $\text{CO}_2$ -Ar have been reported by Huety and Chevalier [84] and Simpson and Chandler [73]. The impact tube measurements



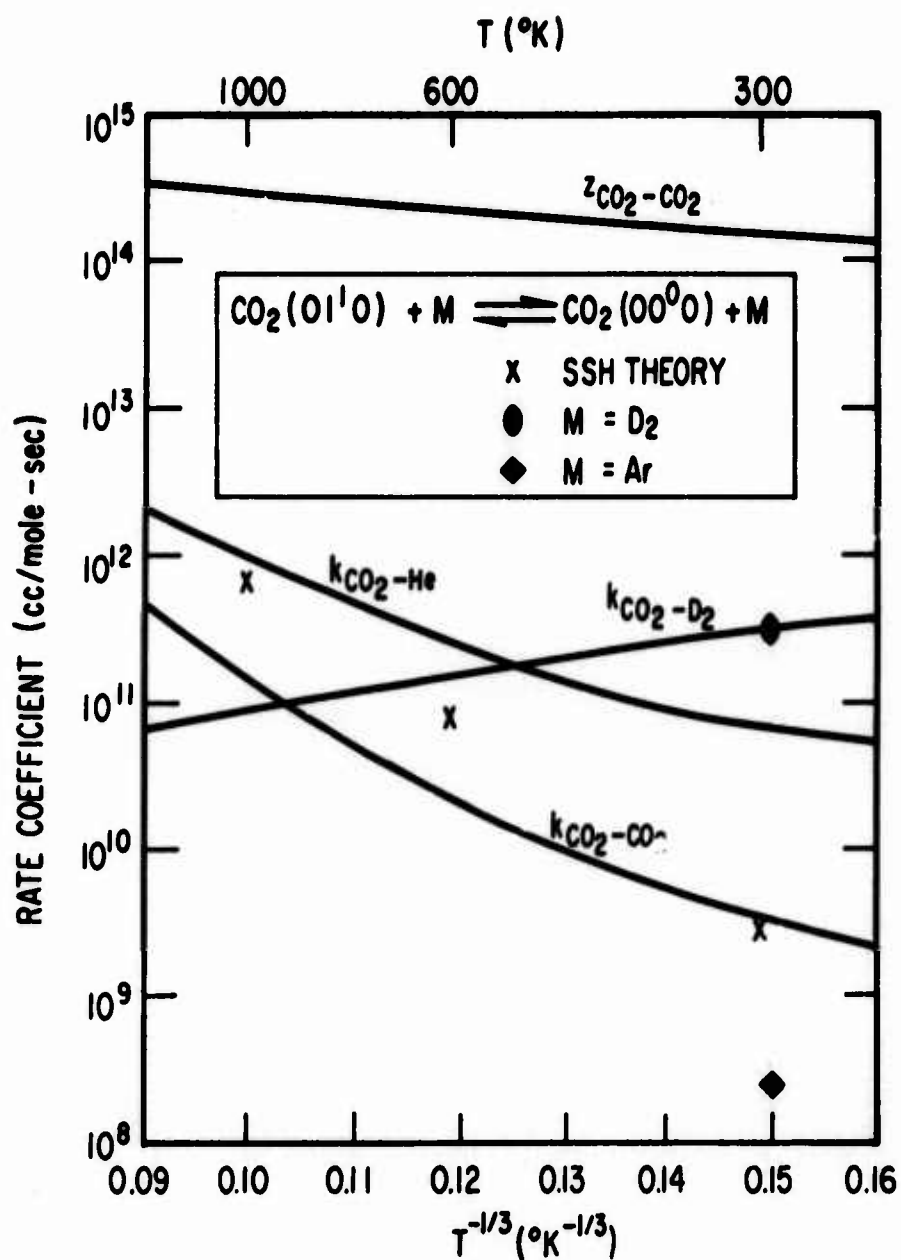
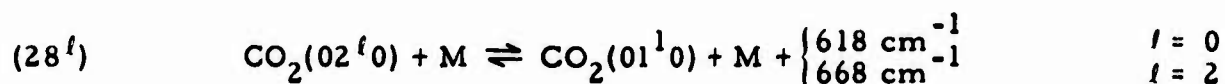
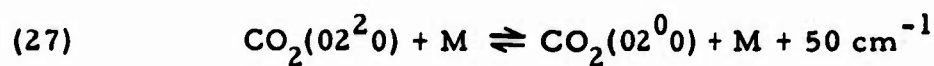
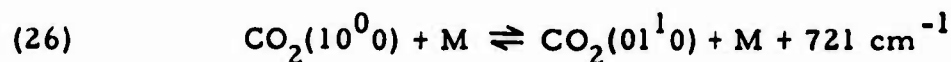
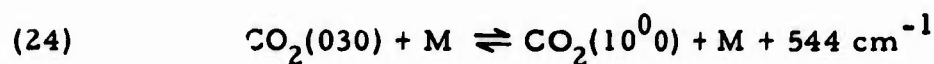
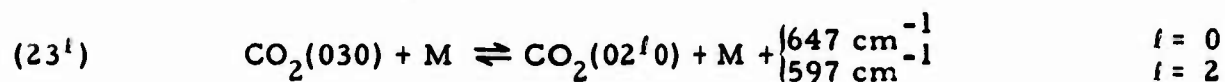
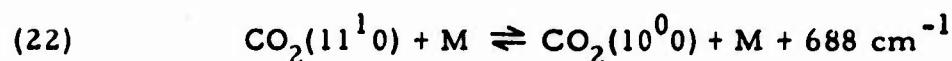
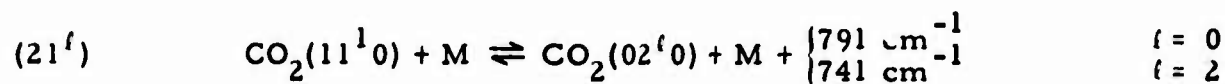


Fig. 6. Experimentally derived rate coefficients for deactivation of  $\text{CO}_2(01^1_0)$  by M: M =  $\text{CO}_2$  and He, Ref. [5];  $\diamond$  Ref. [84],  $\circ$  Ref. [86]; X SSH calculations, Ref. [51].

of Ref. [84] are more consistent with data of other investigators; thus, we take their results and assume Ar to be 6% as efficient as CO<sub>2</sub> in deactivating  $\nu_2$ . Relaxation of  $\nu_2$  by F, F<sub>2</sub>, DF, and D has not been measured. The efficiencies of these species are estimated to be similar to CO<sub>2</sub> with the exception of D, which is assumed similar to D<sub>2</sub>. These are gross approximations, and additional measurements for these species are needed.

#### 4. OTHER REACTIONS

The rates of the remaining reactions have not been measured. These reactions include



Theoretical estimates of the rates of these reactions have been made by Herzfeld [51] for  $M = \text{CO}_2$ . Our analytical approximations of his rates are

$$k_{21}^0 = 8.6 \times 10^{-3} T^{4.19} e^{0.9030}$$

$$k_{21}^2 = 7.9 \times 10^4 T^{2.5} e^{4.410}$$

$$k_{22} = 5.9 T^{3.78} e^{0.5490}$$

$$k_{23}^0 = 3.87 \times 10^2 T^{3.3} e^{1.240}$$

$$k_{23}^2 = 5.7 \times 10^2 T^{3.32} e^{1.220}$$

$$k_{24} = 4.9 \times 10^2 T^{3.04} e^{1.060}$$

$$k_{26a} = 4.4 \times 10^2 T^{3.26} e^{1.480}$$

$$k_{-27} = 5.9 \times 10^8 T^{1.5}$$

$$k_{28a}^0 = 2.4 \times 10^3 T^{3.1} e^{1.40}$$

$$k_{28a}^2 = 6.0 \times 10^2 T^{3.31} e^{1.30}$$

We assume both levels of vibrational angular momentum in (030) are deactivated at the same rate in determining  $k_{23}^1$  and  $k_{24}$ .

Seeber [56] has also calculated  $k_{-27}$  at 300°K, and his value is 35% larger than that of Herzfeld and has been used with the temperature variation calculated by Ref. [51] to determine  $k_{-27}$ .

Reactions (21) through (24) represent collisional mechanisms that may contribute to the population of the lower laser level from products of deexcitation of the upper laser level. Since experimental estimates of the rate of these reactions are not available, we use Herzfeld's rate coefficients and assume the probability for reaction is the same for each species. In addition, we assume that all species are equally efficient in equilibration of the vibrational momentum of (02<sup>f</sup>0), React. (27).

For Reacts. (26) and (28), we use the theoretical rate coefficients of Herzfeld for species  $M_{12}$  (Table IV). Since the temperature variation of React. (29) for  $M_{13}$  and  $M_{14}$  is considerably different from the calculation of Herzfeld, we use the temperature dependence of the rates of React. (29) for these species and adjust the relative rates of the reaction to be in the same ratio as that calculated by Herzfeld for  $\text{CO}_2\text{-CO}_2$  at 1000°K, where the relative magnitude of the calculated rates may be expected to be fairly accurate. At 1000°K for  $\text{CO}_2\text{-CO}_2$ , Herzfeld finds

$$k_{26}:k_{28}^0:k_{28}^2:k_{29} = 1.8:3.4:4.0:1.0$$

Hence, we take

$$k_{26b} = 1.8k_{29b}$$

$$k_{26c} = 1.8k_{29c}$$

$$k_{28b}^0 = 3.4k_{29b}$$

and continue.

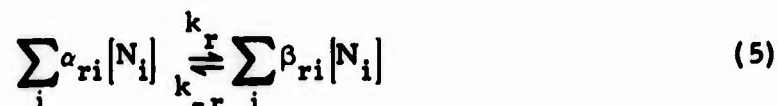
The complete kinetic model for the DF-CO<sub>2</sub> chemical transfer laser is given in Table IV.

## V. COMPUTER EXPERIMENTS

### A. LASER SIMULATION

The chemical laser computer simulation used in this study is described in Ref. [2]. A resume of its features is presented here. Rate equations are used to represent the chemical kinetic and stimulated emission processes occurring in a representative unit volume within a Fabry-Perot cavity. All processes are assumed to be uniform throughout the cavity. Only the  $(00^01)$  -  $(10^00)$  band is permitted to lase, and a Boltzmann distribution of the rotational levels at the translational temperature  $T$  is assumed. Only the transition with maximum gain is assumed to lase, and this is always in the P-branch. During lasing, the gain at line center is held constant at its threshold value  $\alpha_{thr}$ .

The chemical reactions may be written as



where  $[N_i]$  is the molar concentration of species  $i$ ,  $\alpha_{ri}$  and  $\beta_{ri}$  are stoichiometric coefficients, and  $k_{\pm r}$  are the forward and backward rate coefficients.

The rate of change of concentration of  $\text{CO}_2(00^01)$  is given by

$$\frac{d[\text{CO}_2(00^01)]}{dt} = -\chi_{rad}(J) + \chi_{ch}(00^01) \quad (6a)$$

For  $\text{CO}_2(10^0 0)$ , we have

$$\frac{d[\text{CO}_2(10^0 0)]}{dt} = \chi_{\text{rad}}(J) + \chi_{\text{ch}}(10^0 0) \quad (6b)$$

and for all other species

$$\frac{d[N_i]}{dt} = \chi_{\text{ch}}(i) \quad (6c)$$

The photon emission rate  $\chi_{\text{rad}}(J)$  is the rate of change of concentration resulting from lasing, and  $J$  is the rotational quantum number for the lower level of the maximum gain transition within the 10.6- $\mu\text{m}$  band. The rate of change of species concentration resulting from chemical reactions is

$$\chi_{\text{ch}}(i) = \sum_r (\beta_{ri} - \alpha_{ri}) L_r \quad (7)$$

where

$$L_r = k_r \prod_j [N_j]^{\alpha_{rj}} - k_{-r} \prod_j [N_j]^{\beta_{rj}}$$

The laser cavity is assumed to have a uniform photon flux with active medium length  $L$  and mirror reflectivities  $R_0$  and  $R_L$ . Lasing initiates when the highest gain transition of the band is equal to the threshold gain  $\alpha_{\text{thr}}$  where

$$\alpha_{\text{thr}} = -\frac{1}{2L} \ln(R_0 R_L) \quad (8)$$

Only P-branch transitions need be considered; thus, the gain of a transition with lower level J is

$$\alpha(J) = \frac{hN_A}{4\pi} \omega(J) B(J) \phi(J) \left\{ \frac{2J+1}{2J-1} [\text{CO}_2(00^01, J-1)] - [\text{CO}_2(10^00, J)] \right\} \quad (9)$$

where the wave number of the transition is  $\omega(J)$  and  $B(J)$  is the Einstein isotropic absorption coefficient based on the intensity. Line-broadening constants and resonance constants used in the Voigt profile  $\phi(J)$  at line center are those of Ref. [2].

The Boltzmann distribution of the rotational populations is given by

$$[\text{CO}_2(\nu_1, \nu_2^f, \nu_3; J)] = [\text{CO}_2(\nu_1, \nu_2^f, \nu_3)] \frac{(2J+1)}{T/2\theta_r} e^{-hcE_J/kT} \quad (10)$$

where  $T/2\theta_r$  is the rotational partition function, the additional factor of 2 is a statistical symmetry factor,  $\theta_r$  is the characteristic rotational temperature [2], and rotational energy  $E_J$  is from Herzberg [20]. We note that only odd J values are present in the upper states and even values in the lower states. Planck's constant, the speed of light, and Boltzmann's constant are denoted as h, c, and k, respectively. The energy equation for a constant density gas is written in the form

$$\sum_i [N_i] C_{pi} \frac{dT}{dt} - \frac{dp}{dt} = -P_L - \sum_i \frac{d[N_i]}{dt} H_i \quad (11)$$



where  $C_{pi}$  is the specific heat at constant pressure,  $H_i$  is the molar enthalpy of species  $i$ ,  $p$  is the pressure, and  $P_L$  is the output lasing power per unit volume given by

$$P_L(t) = hcN_A \omega(J) \chi_{rad}(J) \quad (12)$$

The average intensity inside the cavity may be calculated from the relation

$$I = P_L(t)L/(1 - \sqrt{R_0 R_L})$$

A fourth-order Runge-Kutta routine is used to solve Eqs. (6), (11), and the equation of state to determine pressure, temperature, and species concentrations until, at some time  $t_0$  and for some value  $J = J_0$ , the gain on a given vibration-rotation transition reaches  $\alpha_{thr}$ . At this time, the laser pulse begins. Then Eqs. (6), (8), (11), (12), and the equation of state are solved for the transient temperature, pressure, concentrations, output power, and active  $J$ . During lasing, this value of  $J$  shifts as a result of the temperature rise and concentration changes. Lasing terminates when all gains drop below  $\alpha_{thr}$ .

The pulse energy per unit volume is given by

$$E = \int_{t_0}^{t_0+t_c} P_L dt \quad (13)$$

where  $t_c$  is the pulse duration. For simplicity, initiation is modeled by the introduction of a finite concentration of F atoms into the initial gas mixture.

#### B. CHEMICAL, COLLISIONAL, AND CAVITY MECHANISMS

The relative importances of the various kinetic processes are examined by simulating laser performance at typical laboratory conditions. Two initial gas mixtures of  $\text{XF}:1\text{F}_2:1\text{D}_2:40\text{He}:8\text{CO}_2$  at  $300^\circ\text{K}$  and 50 torr with  $X = 0.1$  and 0.01 are used, where the F atoms represent varying degrees of dissociation of  $\text{F}_2$  by some initiation method. Mirror reflectivities are 0.9 and 1.0, and the active medium length is 53.3 cm. The following paragraphs give an interpretation of the principal kinetic mechanisms of these cases.

By noting the conservation of vibrational quanta in  $\text{DF}(v)$  and properly accounting for the vibrational levels, one may deduce the relation

$$\sum_{v=1}^9 vP_v = \sum_{v=1}^9 T_v + \sum_{v=1}^9 v \frac{d\text{DF}(v)}{dt} + \sum_{v=1}^9 D_{v,v-1} \quad (14)$$

where  $P_v$  is the rate of pumping into level  $v$  by Reacts. (4) and (5),  $T_v$  is the rate of transfer from  $\text{DF}(v)$  to  $\text{CO}_2(00^01)$  by React. (10),  $d\text{DF}(v)/dt$  is the rate of change of the  $\text{DF}(v)$  concentration, and  $D_{v,v-1}$  is the total rate of

deactivation of  $DF(v)$  to  $DF(v-1)$  by Reacts. (6) and (8).<sup>2</sup> The terms in Eq. (14) may be interpreted as

$$\left[ \begin{array}{c} \text{Chemical} \\ \text{pumping} \\ \text{rate} \end{array} \right] = \left[ \begin{array}{c} \text{Collisional} \\ \text{transfer} \\ \text{rate} \end{array} \right] + \left[ \begin{array}{c} \text{Level filling} \\ \text{rate in DF} \end{array} \right] + \left[ \begin{array}{c} \text{Collisional} \\ \text{deactivation} \\ \text{rate of DF} \end{array} \right]$$

The rate of excitation of  $CO_2(00^0 1)$  by  $DF(v)$  is equal to the transfer rate; therefore, conservation of number density of  $CO_2(00^0 1)$  may be expressed as

$$\sum_{v=1}^9 T_v = \frac{d[CO_2(00^0 1)]}{dt} + D_C + \chi_{rad}(J) \quad (15)$$

where  $D_C$  is the rate of collisional deactivation of  $(00^0 1)$ .

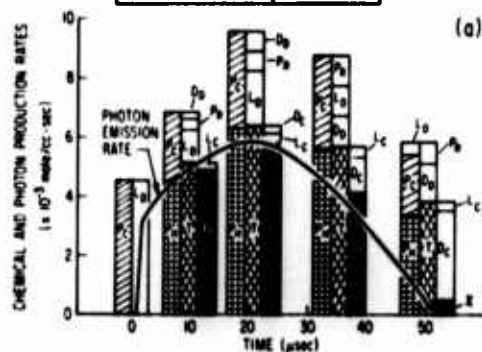
The relative importance of these mechanisms throughout the pulse is graphically illustrated in Fig. 7. An abbreviated notation for the terms in Eqs. (14) and (15) is used where the contribution from the pumping React. (4) for  $v = 1, \dots, 4$  is referred to as  $P_C$ . For  $v \geq 5$ , React. (4) normally transfers matter in the reverse direction and is denoted as  $P_R$ . The contribution from React. (5) is labelled  $P_H$ . The total rate of collisional deactivation of  $DF(v)$  is denoted by  $D_D$ . The total collisional transfer rate is  $T$ , and the rates of level filling for  $DF(v)$  and  $CO_2(00^0 1)$  are denoted as  $L_D$  and  $L_C$ , respectively.

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<sup>2</sup>The rate of React. (3) is normally too small to contribute to this term, and the number of quanta is not changed by the VV processes, React. (7).

$C_2P_C$  : PUMPING OF DF BY (REACTS 4a-4d)  
 $P_R$  : REVERSE OF PUMPING BY (REACTS 4a-4f)  
 $(III) P_H$  : PUMPING OF DF BY (REACT (5))  
 $CO_2 T$  :  $DF \cdot CO_2$  TRANSFER  
 $D_D$  : DEACTIVATION OF DF  
 $D_C$  : DEACTIVATION OF  $CO_2$   
 $L_D$  : LEVEL FILLING OF DF  
 $L_C$  : LEVEL FILLING OF  $CO_2$   
 $X$  : PHOTON EMISSION RATE  $X_{rad}$

INITIAL CONDITIONS						CAVITY	
F	F <sub>2</sub>	D <sub>2</sub>	CO <sub>2</sub>	HE		L	53.3 cm
0.1	1	1	8	40		R <sub>L</sub>	10
						R <sub>0</sub>	0.9
P <sub>i</sub> : 50 Torr							
T <sub>i</sub> : 300°K							



INITIAL CONDITIONS						CAVITY	
F	F <sub>2</sub>	D <sub>2</sub>	CO <sub>2</sub>	HE		L	53.3 cm
0.01	1	1	8	40		R <sub>L</sub>	10
						R <sub>0</sub>	0.9
P <sub>i</sub> : 50 Torr							
T <sub>i</sub> : 300°K							

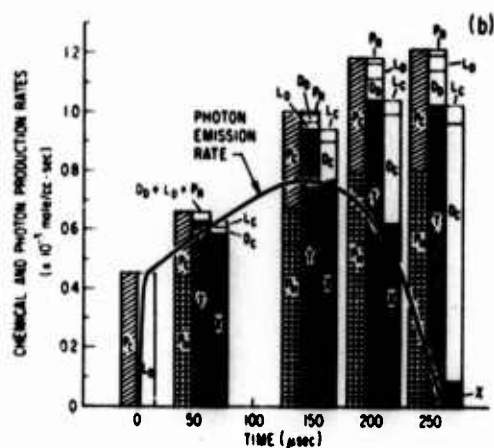


Fig. 7. Relationship of dominant kinetic mechanisms in the DF- $CO_2$  model. (a) Initial  $F = 0.1$ .  
 (b) Initial  $F = 0.01$ .

We examine the mechanisms for  $F = 0.1$ , Fig. 7a, in detail and point out only those features that are different for  $F = 0.01$  (Fig. 7b). Approximately 60% of the initial  $F$  atom concentration is consumed in the first few microseconds by React. (4),  $P_C$ . During this period,  $D$  atoms are produced, and the vibrational levels of  $DF(v)$  begin filling. During this transient, the rate of React. (5) increases with onset of operation of the chain, and transfer to  $CO_2(00^0 1)$  is followed by emission of lasing photons when cavity threshold is reached. After the large initial consumption of  $F$  atoms, the concentration of  $F$  atoms increases slowly and monotonically, and we have quasisteady chain operation such that

$$[F]_{t=0} = [F]_{t \geq 0} + [D]_{t \geq 0}$$

Time histories of species concentrations for initial  $F = 0.1$  are shown in Fig. 8.

The rate of level filling in  $DF$ ,  $L_D$ , represents a rate of energy storage. Some of this stored energy is lost to collisional deactivation at a later time. From Fig. 7a, we see that only a small quantity of the stored energy in  $DF$  is available at pulse termination. A small rate of level filling in  $CO_2(00^0 1)$ ,  $L_C$ , is required to maintain the necessary gain, Eq. (8). This rate is coupled to the rate of deactivation of the lower level,  $\chi_{rad}(J)$ ,  $D_C$ , and the transfer rate.

Lasing continues until the rate of transfer into  $(00^0 1)$  is not sufficient to offset the loss mechanisms, and all  $\alpha(J)$  drop below  $\alpha_{thr}$ . Pulse termination is caused in part by three processes. First, depletion of the fuel

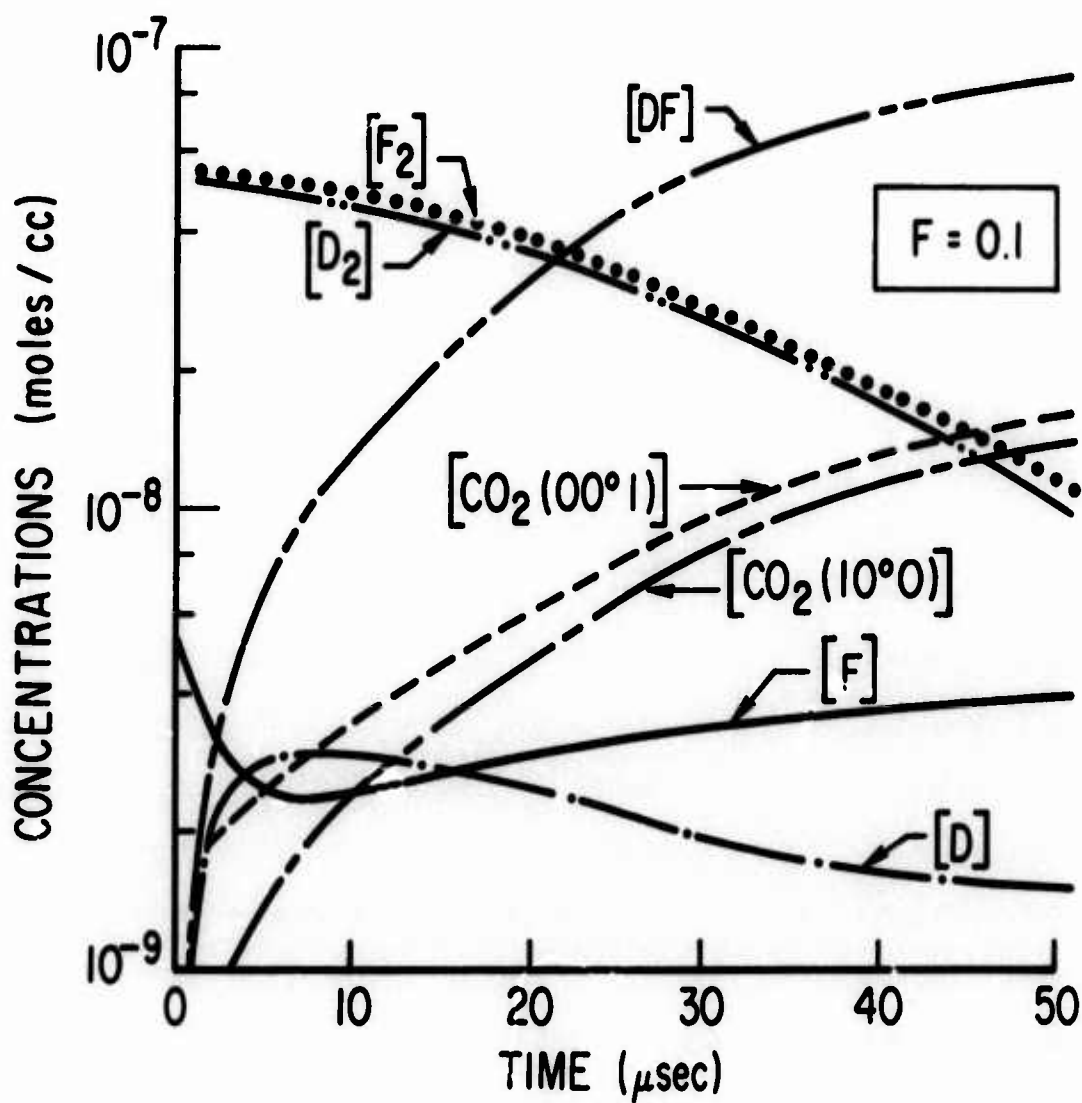


Fig. 8. Time histories of species concentrations for initial  $F = 0.1$ .

supply ( $D_2$  and  $F_2$ ) results in a lower mass transfer rate for Reacts. (4) and (5); this is not the case for  $F = 0.01$ . Second, deactivation of  $DF(v)$  and of  $CO_2(00^01)$  by Reacts. (18) and (19) increases sharply near pulse termination because of the increasing  $DF$  and  $CO_2(00^01)$  concentrations. Recall that  $DF$  is a very efficient collisional deactivator for both  $DF(v)$  and  $CO_2(00^01)$ . Third, the temperature rise resulting from the exothermic chain reaction gives rise to higher concentrations in the  $(01^10)$  and  $(02^10)$  levels of  $CO_2$ ; therefore, depletion of the lower laser level is less efficient.

The principal differences in mechanisms for the two values of initiation are easily seen in Figs. 7a and 7b. With the higher pumping rate for  $F = 0.1$ , the transfer rate is not fast enough to deplete the excited levels of  $DF$ ; hence, the rate of level filling is higher and a larger  $DF(v)$  population results in higher deactivation losses in  $DF$ . Pumping for  $F = 0.01$  is slower and is still increasing when the pulse terminates. Although transfer to  $CO_2$  is more efficient with this lower pumping rate, only 50% of the fuel is consumed before pulse termination, as compared to 80% for  $F = 0.1$ . Although deactivation in  $CO_2$  is more important for  $F = 0.01$  and is the cause of pulse termination, this is partly offset by the lower rate of deactivation of  $DF$ .<sup>3</sup> Hence, even with much less of the fuel consumed during the pulse, the chemical efficiency for  $F = 0.01$  is 6% as compared to 8% for  $F = 0.1$ . A more detailed investigation of these mechanisms is now given.

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<sup>3</sup> Lower levels of initiation are often found to give rise to increased importance of mechanisms deactivating the lasing species [43].

In Fig. 9, the time histories of the rate  $L_r$  of DF(v) deactivation reactions are shown. For  $F = 0.1$ , the rapid production of DF(v) in the upper vibrational levels after initiation leads to deactivation of DF by the DF-D<sub>2</sub> VV React. (8). This rate eventually decreases as the concentration of D<sub>2</sub>(v) (v > 0) increases relative to DF(v), until the reaction begins to run in reverse near termination, as shown by the dashed curve. The principal catalysts deactivating DF are F and D, React. (6e), and self-relaxation of DF, React. (6c). Catalysts of other VT mechanisms included in the figure are CO<sub>2</sub>, React. (6a), He, React. (6b); and D<sub>2</sub>, React. (6d).

A lower overall rate of DF deactivation is found when initial  $F = 0.01$ , and React. (6e) is less significant as a result of the lower F and D concentrations. A slower DF-D<sub>2</sub> VV transfer rate, React. (8), is also found.

With initial  $F = 0.1$ , the dominant deactivation catalyst for CO<sub>2</sub>(00<sup>0</sup>1) is DF, React. (18c), in Fig. 10. The catalyst for this reaction also contains F and D<sub>2</sub>; however, the contribution of these species is at least one order of magnitude less than that of DF for most of the pulse duration. The high concentrations of He and CO<sub>2</sub> cause significant deactivation by Reacts. (18b) and (18a). As a result of our earlier assumption, the relative rates of React. (19) are very similar to those of (18). These deactivation mechanisms are very similar for  $F = 0.01$ , although the rate is lower as a result of the slower transfer rate and a lower concentration in (00<sup>0</sup>1).

The principal mechanism populating the lower lasing level (10<sup>0</sup>0) is laser action,  $\chi_{rad}(J)$ , Fig. 11. Reactions (13), (22), and (24) deactivate (11<sup>1</sup>0) and (030); these levels are supplied by deactivation of (00<sup>0</sup>1) through



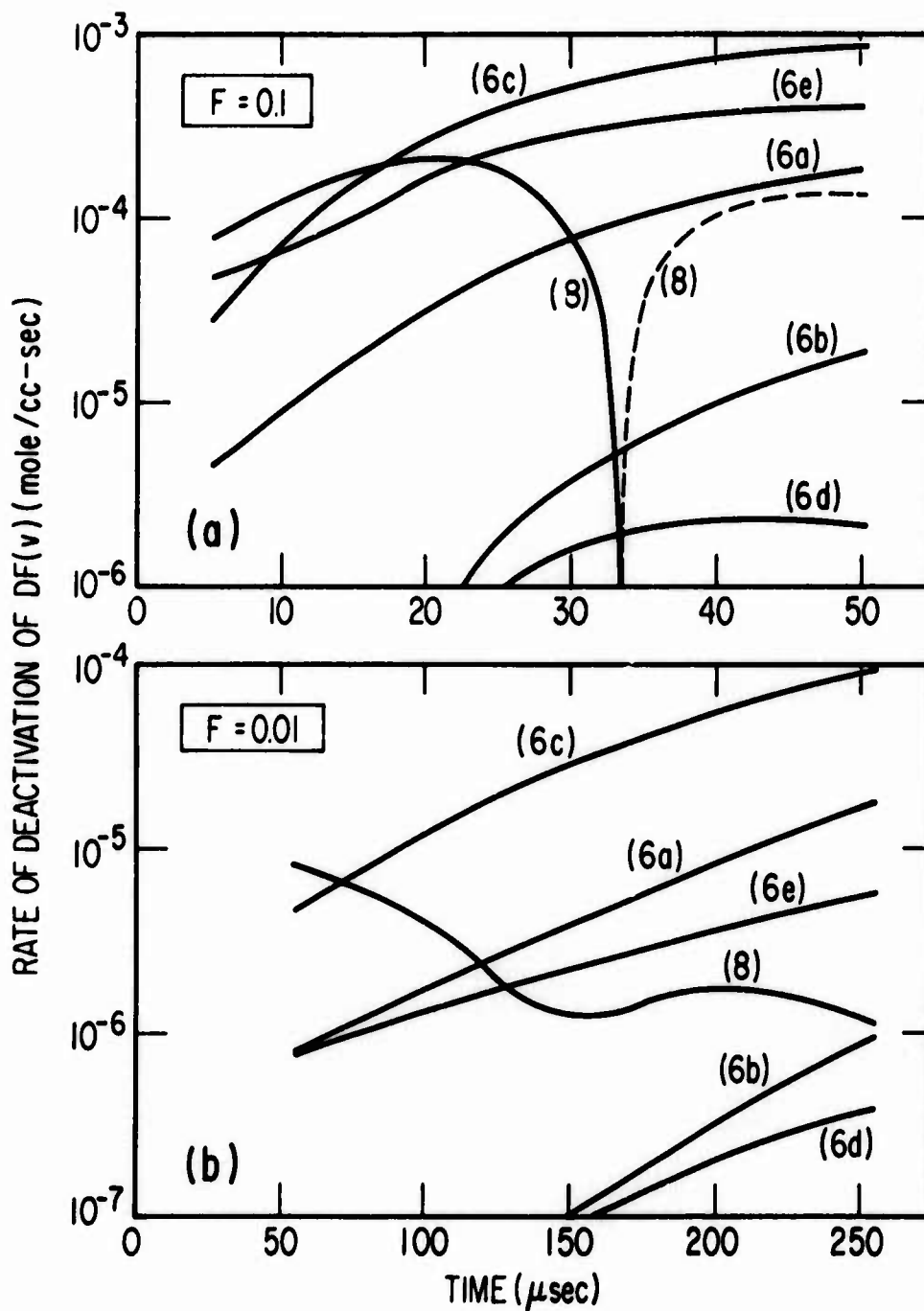


Fig. 9. Time history of the rate  $L_R$  of important processes deactivating  $DF(v)$ . (a) Initial  $F = 0.1$ . (b) Initial  $F = 0.01$ .

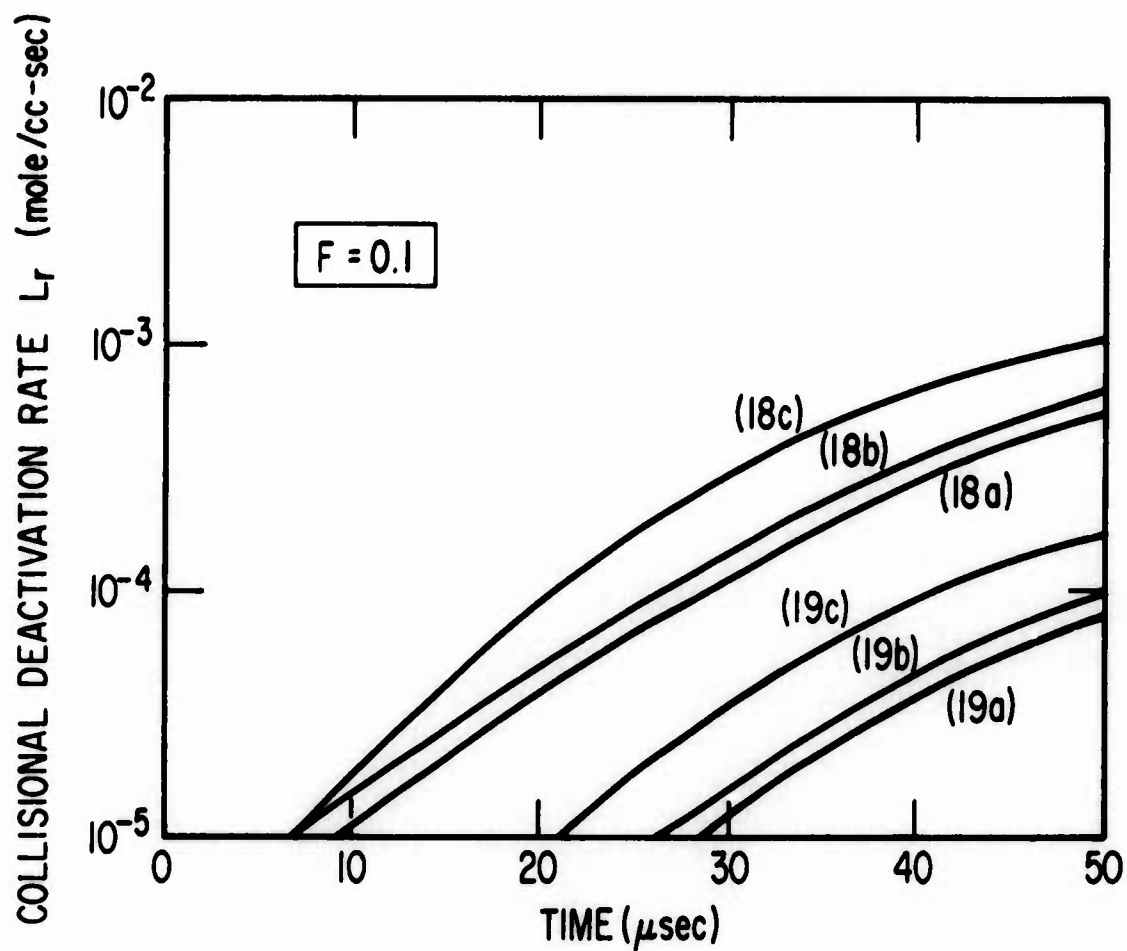


Fig. 10. Time history of the rate  $L_r$  of reactions deactivating the upper laser level.

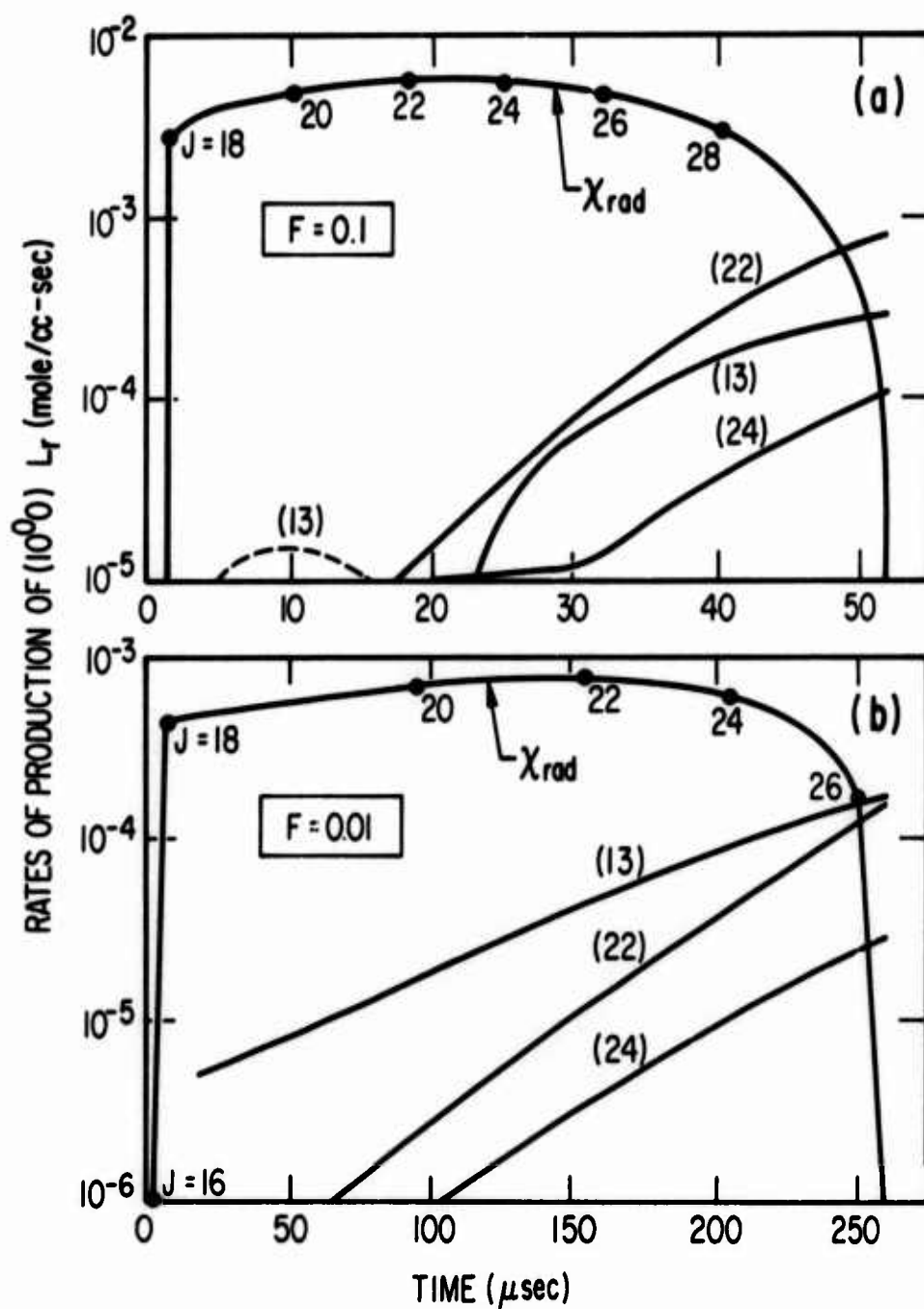


Fig. 11. Kinetic mechanisms that produce  $\text{CO}_2(10^0_0)$ . The time of a shift in the lasing transition to a new value of  $J$  is labeled with the new  $J$ . (a) Initial  $F = 0.1$ . (b) Initial  $F = 0.01$ .

Reacts. (18) and (19). The increased rate of React. (13) relative to Reacts. (22) and (24) for  $F = 0.01$ , as compared to  $F = 0.1$ , is a result of the slower rate of transfer to  $(00^0_1)$  and thus a lower concentration in this level and a higher concentration in the ground state.

Collisional processes that deactivate the lower laser level for  $F = 0.1$ , Fig. 12, and for  $F = 0.01$  are similar. Deactivation of  $(10^0_0)$  to  $(02^f_0)$  through React.  $(25^f)$  is the major mechanism that empties the lower level. The intramolecular VV reaction  $(10^0_0) \rightarrow (01^1_0)$ , React. (26), is also an important process, especially for  $M = \text{He}$ , React.  $(26b)$ . The decrease during the reaction in the efficiency of the intermolecular VV process, React. (16), is a result of the increase in temperature and equilibrium population of  $(01^1_0)$ .

Since deactivation of  $(10^0_0)$  is closely linked to the  $(02^f_0)$  levels which in turn deactivate through  $(01^1_0)$  to the ground state, we examine those processes that depopulate  $(02^f_0)$  in Fig. 13 for  $F = 0.1$ . Again, He is the principal deactivation catalyst, React.  $(28^f_b)$ . Other intramolecular VV catalysts  $\text{CO}_2$ , Reacts  $(28^f_a)$ , and  $\text{D}_2$  and  $\text{D}$ , React.  $(28^f_c)$ , contribute very little to the equilibration of these levels. Reactions  $(17^f)$  are significant early in the pulse as VV deactivation processes, but near termination the increased population of  $(01^1_0)$  and the higher temperature cause these reactions to transfer matter in the reverse direction. The relative rates of these reactions for initial  $F = 0.01$  are similar to those shown in Fig. 13.

In the present model, deactivation rate coefficients for  $(02^f_0)$  by VT and intramolecular VV processes are based on measurements of VT

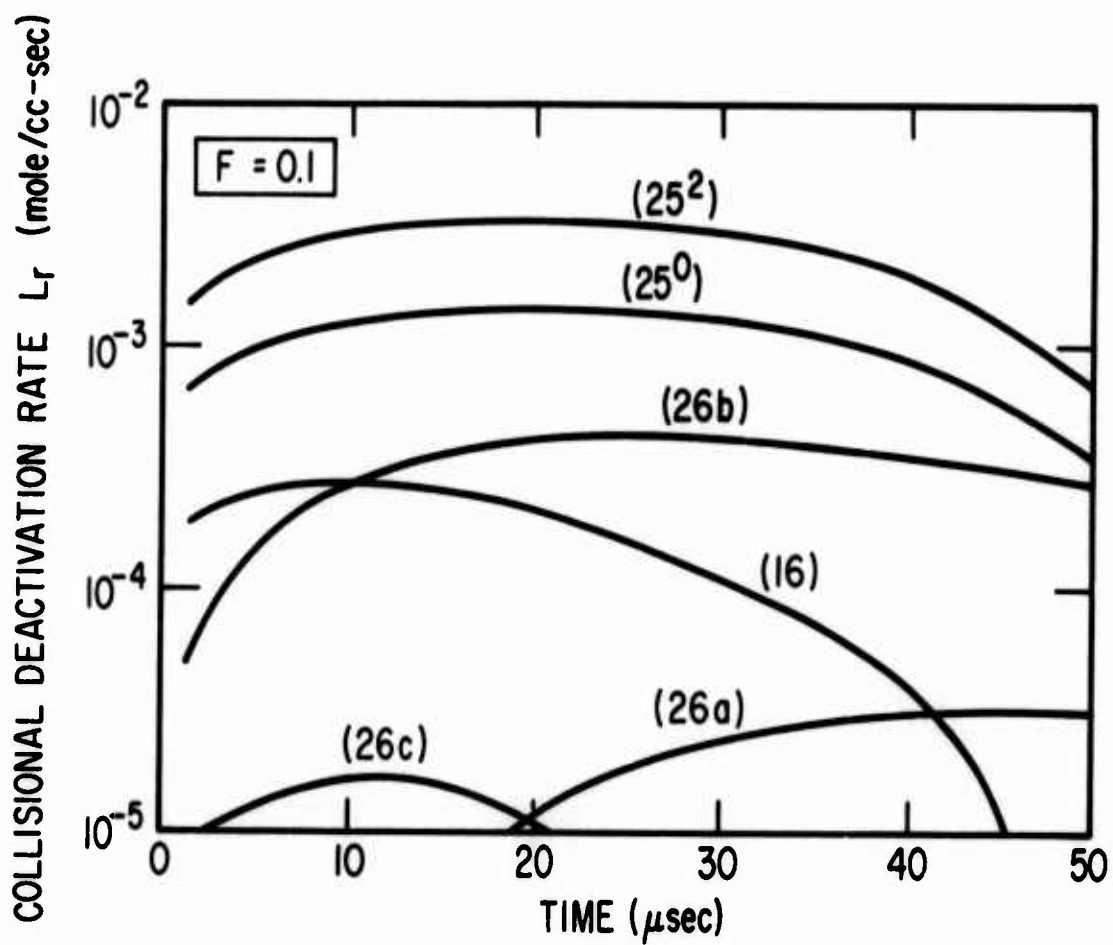


Fig. 12. Kinetic mechanisms that empty  $\text{CO}_2(10^0_0)$ .

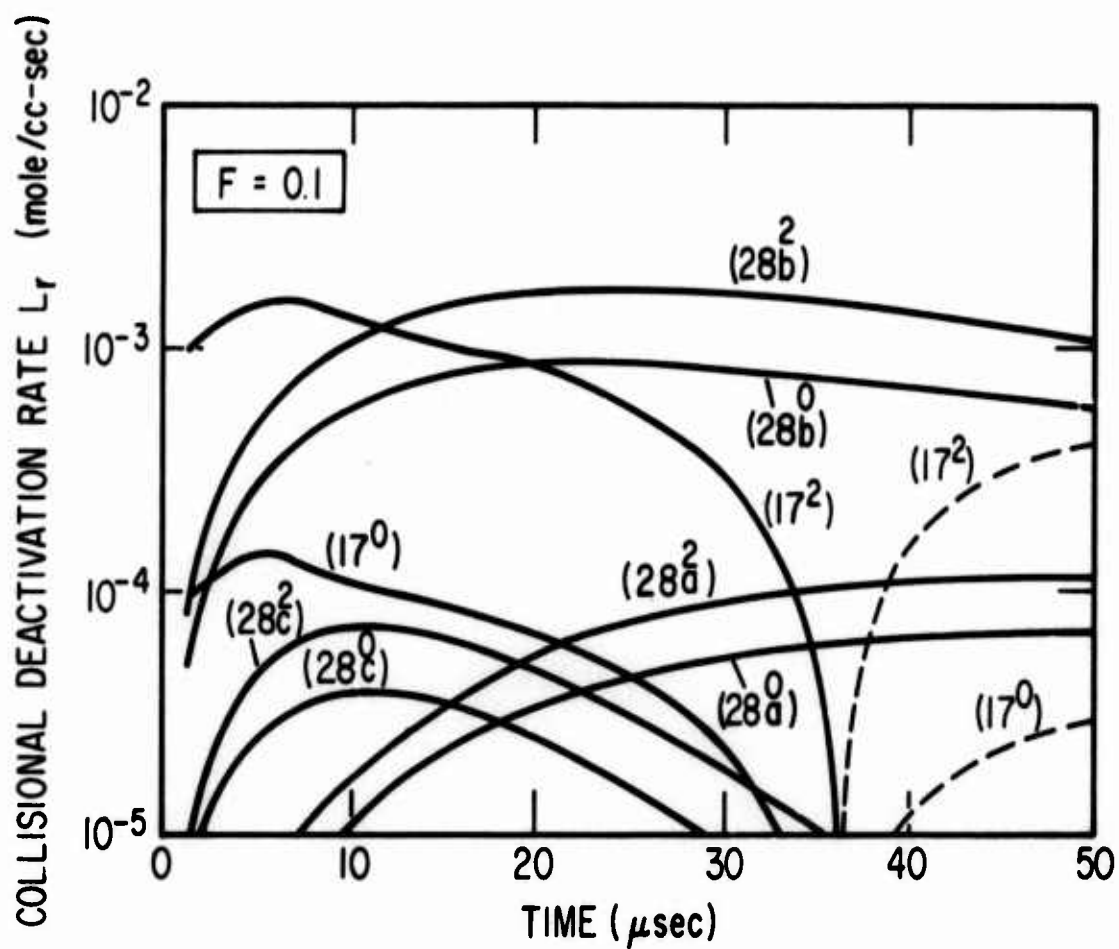


Fig. 13. Collisional processes that equilibrate  $(02^1_0)$ .

deactivation of  $(01^1_0)$ . Therefore, the VT mechanisms that equilibrate  $(01^1_0)$ , React. (29), are comparable in importance to the corresponding VT mechanisms that equilibrate  $(02^1_0)$ , React. (28<sup>f</sup>). For the mixtures considered in this study, we also find that state  $(10^0_0)$  and all levels below it are very near equilibrium throughout the reaction.

### C. EFFECT OF VARIATIONS IN UNCERTAIN RATE COEFFICIENTS

The variations in rate coefficients from the standard are selected to include the major uncertainties, at the time of this study (early 1972), in rates of dominant processes. Of course, the degree of uncertainty of a rate coefficient is only speculative and significant changes in the initial mixture composition can change the relative importance of dominant mechanisms. Hence, the following variations only give an indication of the sensitivity of laser performance to some of the more important mechanisms. The effect of these changes on the peak power  $P_{L_{max}}$ , pulse energy, and pulse duration are shown in Table V.

The variations from the standard model (Table IV) studied and their principal effects are:

- Rate 1     The rate of  $DF-CO_2$  transfer, React. (10), is assumed constant in temperature and equal to  $3.82 \times 10^{12}$  cc/mole-sec for all  $DF(v)$ . There is some evidence that the negative temperature dependence in the standard model is too strong [87]. When the pumping rate is large relative to the transfer rate, larger deactivation losses occur before transfer from  $DF(v)$  to  $CO_2$  takes place. With  $k_{10}$  assumed constant, deactivation losses

Table V. Effect of Rate Coefficient Changes on Pulse Characteristics

Rate	F = 0.1			F = 0.01		
	P <sub>L</sub> max (Watts/cc)	E (joule/liter)	t <sub>0</sub> + t <sub>c</sub> (μsec) <sup>a</sup>	P <sub>L</sub> max (Watts/cc)	E (joule/liter)	t <sub>0</sub> + t <sub>c</sub> (μsec) <sup>a</sup>
Standard	65.9	2.33	52.0	8.64	1.71	260
1	86.4	3.04	52.4	9.12	1.82	266
2	104.5	3.49	50.3	9.55	1.91	267
3	65.9	2.35	52.1	8.64	1.70	260
4	66.9	2.70	61.7	9.11	2.05	303
5	65.0	2.29	51.9	8.64	1.71	260
6	65.9	2.33	51.6	8.64	1.70	260
7	63.2	1.94	43.1	7.46	1.25	215
8	108.0	2.32	34.14	17.81	2.07	156
9	70.3	2.65	55.4	9.73	2.02	275
10	67.9	2.42	52.3	8.71	1.73	262
11	59.1	1.81	43.8	8.48	1.66	257
12	64.7	2.18	48.6	8.38	1.61	252
13	66.5	2.37	52.8	8.68	1.72	261

<sup>a</sup> The exact value of t<sub>0</sub> was not determined for each calculation. Typical values of t<sub>0</sub> are 1 and 5 μsec for F=0.1 and 0.01, respectively, and t<sub>0</sub> is normally independent of deactivation mechanisms.



in DF are reduced. Hence, this change gives higher values for the pulse energy and peak power, and the effect is larger for  $F = 0.1$  where the pumping rate is higher.

- Rate 2    Transfer for DF(1) is the same as for Rate 1 and  $k_{10v} = vk_{10_1}$ . Preliminary experimental evidence indicates that the rate of transfer may increase with  $v$  [87]. By comparing these results with those of Rate 1, both  $P_{L_{max}}$  and  $E$  increase with this change, especially for  $F = 0.1$ . The competition between deactivation in DF and transfer to  $CO_2$  indicated earlier is responsible for this behavior.
- Rate 3    The efficiency of deactivation of  $(00^01)$  by  $D_2$  and  $F$ , React. (18) and (19), is assumed the same as  $CO_2-CO_2$ . The laser pulse characteristics are insensitive to these reactions for our choice of initial concentrations.
- Rate 4    Rate 3 is modified such that the efficiency of DF in deactivating  $(00^01)$  is proportional to  $T^{-2}$  as indicated by combining results of Ref. [35] with preliminary results of Cool at  $300^\circ K$  [47]. Of course, this change gives rise to an increase in  $E$  and  $P_{L_{max}}$ , since deactivation is important later in the reaction when the temperature and the DF concentration are both higher.
- Rate 5    The rate coefficients for all processes that deactivate  $(10^00)$  are arbitrarily reduced by a factor of 10. This decrease was not sufficient to cause  $(10^00)$  to deviate from near equilibrium; therefore, the pulse characteristics are essentially the same

as those computed with the standard rate. A much larger decrease in these rate coefficients is necessary before pulse characteristics are substantially altered.

- Rate 6 Rate coefficients for Reacts. (13), (22), and (24) are increased by a factor of 10. This change is not large enough to prevent the reactions that relax ( $10^0$ ) from maintaining the near equilibrium condition; thus, no change is found in pulse characteristics.
- Rate 7 Rate coefficients for all processes in Reacts. (18) and (19) are arbitrarily increased by a factor of 2. This pessimistic change is greater than the uncertainty in the rates of these processes and causes a reduction in  $P_{Lmax}$ ,  $E$ , and  $t_0 + t_c$ .
- Rate 8 The overall pumping rates  $k_4$  and  $k_5$  are increased by a factor of 2. As expected,  $P_{Lmax}$  increases and the pulse duration decreases with the faster chain. Again, the competition between deactivation in DF and transfer to  $CO_2$  manifests itself, and no increase in  $E$  for  $F = 0.1$  is shown while  $E$  increases for  $F = 0.01$  where this competition is less.
- Rate 9 The distribution of  $D + F_2$  pumping, Reacts. (5), are assumed to be more sharply peaked near  $v = 8$ . The new distribution is obtained from Herbelin's new interpretation [88] of recent  $H + F_2$  data of Jonathan and co-workers on the basis of revised estimates of the HF matrix elements. The altered distribution is

$$k_5(0): k_5(1): k_5(2): k_5(3): k_5(4): k_5(5): k_5(6): k_5(7): k_5(8): k_5(9) = \\ 0:0.052:0.065:0.078:0.078:0.208:0.494:0.792: 1.0:0.701$$

With this distribution, React. (5) converts 53% of the available chemical energy into vibrational energy; the standard rate converts 46% of this energy. The values of  $P_{Lmax}$ ,  $E$ , and  $t_0 + t_c$  all increase with this change as expected.

- Rate 10 All DF-DF VV rate coefficients are taken as 1/4th the binary collision rate. Preliminary experimental measurements by Bott [87] indicate that these rate coefficients may be this large. As in the HF system [43, 44], laser performance is insensitive to these processes.
- Rate 11 The rate coefficient for deactivation of DF(v) by D and F is increased by a factor of 10. The effect of this rate increase is more important for  $F = 0.1$  where the F and D concentrations are larger.
- Rate 12 The efficiency of  $CO_2$  in deactivating DF is increased by a factor of 10. For these mixture compositions, this change produces a very small decrease in the laser performance characteristics.
- Rate 13 The DF- $D_2$  VV rate coefficients, React.(8), are increased by a factor of 10. Laser performance for these concentrations is insensitive to these reactions.

## VI. SUMMARY AND CONCLUSIONS

A kinetic model of a DF-CO<sub>2</sub> chemical transfer laser and a review of the rate coefficient literature needed to formulate this model are presented. The D<sub>2</sub>+F<sub>2</sub> portion of this model is applicable for modeling the DF chemical laser. Rate coefficients recommended for the model are listed in Table IV. A computer simulation is used to examine the relative importance of various kinetic mechanisms during lasing. Two initial mixture compositions of XF : 1 F<sub>2</sub> : 1 D<sub>2</sub> : 8 CO<sub>2</sub> : 40 He at 50 torr and 300°K, with initiation levels modeled by setting X = 0.1 and 0.01, are studied. For F = 0.01, a 260-μsec pulse with 6% chemical efficiency is predicted, while the higher level of initiation produces a 52-μsec pulse with 8% chemical efficiency. To the best of our knowledge, this is the first published calculation of a CO<sub>2</sub> lasing system that includes detailed modeling of the rate processes that relax the lower laser level. For the initial compositions considered, the (10<sup>0</sup>0) level and those below it are near equilibrium. Calculations with other compositions, however, indicate that this is not always true and detailed modeling is sometimes necessary.

The sensitivity of laser performance to variations in uncertain rate coefficients is shown and rate coefficient measurements critical to improved modeling are indicated. The uncertain rate coefficients for the more important mechanisms include:

1. Rate of deactivation of DF(v) by D and F.
2. Overall pumping rate and distribution into vibrational levels of DF by F + D<sub>2</sub> and D + F<sub>2</sub>.

3. Rate coefficient for transfer from DF(v) to  $\text{CO}_2(00^01)$  as a function of T and v.
4. Rate coefficient for collisional deactivation of  $\text{CO}_2(00^01)$  by DF over a wide temperature range.
5. Rate coefficient for most of the intermolecular and intramolecular VV reactions in  $\text{CO}_2$  involving levels  $(11^10)$ ,  $(03^10)$ ,  $(10^00)$ , and  $(02^10)$ .

Additional measurements and theoretical estimates of these rate coefficients will improve the ability of theoretical laser models to predict laser performance.

Many of the recommended rate coefficients are tentative and subject to reevaluation as more data become available. Nevertheless, the relationship of pumping, transfer, deactivation, and lasing and the competition between deactivation of DF and transfer to  $\text{CO}_2$  has been clearly revealed by these calculations.

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